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MODIFICATION OF THE AATCC CROCKMETER FOR YARN TESTING

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INTRODUCTION

THE crockmeter in current use is substantially the same as when it was first introduced.

Durfee (*1*) describes the early thinking that preceded the development of the instrument in warm personal retrospect by noting that, prior to 1935, crocking was evaluated by rubbing the test fabric with a white cotton cloth placed over the forefinger or thumb. A four-inch length of rub was considered standard. He states that Dr Meyer attracted considerable interest by being able to produce *neat, round spots* in crock test by wrapping white cotton cloth on the small end of a laboratory-flask rubber stopper, fastened by a ring surrounding it and pressed onto the tapered shape of the stopper, and then rubbing the test cloth. Durfee credits Appel with devising a machine to move the rubber stopper four inches and repeat, with a weight to press the stopper as much as desired.

The literature indicates that Durfee designed and built the first crockmeter (*2*) in 1936 with the following features: a wood dowel finger ⅝-inch diameter (flat on botton), 4-inch length of stroke, and a 32-ounce weight on the crocking finger. Unsized white cotton cloth was placed over the finger and clamped on with a ring. Twenty double strokes were suggested as standard. The instrument was accepted by the AATCC (*3*) in 1936 and standard dyeings were made on wool for use as evaluation standards. The rate of rubbing was specified as "one turn per second with rubbing applied oblique to the warp and filling."

Standard spots for the evaluation of crocking (*4*) were set up in 1937 with an attempt to introduce a numerical rating. In 1937, Durfee (*5*) pointed out the need for proper light and viewing angle when judging crocking, and very dramatically demonstrated the transfer of fiber substance to the white cloth in crock tests by running an extended crock test on a white wool cloth and then dyeing the white cotton test square with an acid color. The invisible spot originally produced became heavily colored.

In 1947, Millson, Watkins and Royer (*6*), in their classic work relating crocking to dye techniques, described a two-fingered crockmeter devised by Scanlon. This permitted them to run two crock tests—one wet, the other dry — simultaneously. Later in the same year (*7*) the AATCC introduced the Duplex Crockmeter, a two-fingered instrument differing from the Scanlon modification in that the AATCC machine was essentially two crockmeters run by a common handle, while the Scanlon machine consisted of one arm containing two fingers.

The New York Section of the AATCC (*8, 18*) describes a mechanized crockmeter, developed by the laboratories of the Interchemical Corporation, with facilities for control of temperature, relative humidity and tension on the test fabric. The driving motor is controlled by means of a preset counter, which switches off the machine after a predetermined number of cycles.

The crockmeter with its various refinements to date still presents problems to those who attempt to use it for testing yarns. The AATCC test method (*9*) states that "Yarn can usually be tested by the standard cloth crockmeter satisfactorily after the operator of the test has acquired some training or skill in holding the yarn tight while under test. This is done on yarn in skein form with the aid of a suitable anchor hook between the skein and the test machine. Yarn may also be tested by knitting into a compact, smooth fabric or yarn can be tightly wound on a cardboard." The knitting of yarn into a fabric is time consuming and requires a fairly large, continuous yarn sample, which often is not available. The use of the anchor hook or the cardboard winding methods have a drawback in that, after a very few rubbing cycles, the finger tends to dig in between the yarns, pushing them aside. This results in the finger ultimately rubbing against the abrasive paper or the cardboard.

A search of the literature for possible alternate techniques or apparatus brought out several points of interest. Bean and Rowe (*10*), in 1929, used the hand - rubbing technique and came to the conclusion that "differences in crock fastness could be established more definitely from the number of strokes required to produce a clearly visible stain, rather than by comparing the depth of stain produced by a given number of strokes." This concept of varying the number of strokes to produce a standard level of stain is thought provoking.

Steward (*13*), in 1935, devised a drum on which yarn was evenly wound by means of a transversing arrangement. This drum was rotated at 340 rpm with a shoe covered with white cotton cloth held against it for a total contact time of 12 seconds. Crocking results were translated into numerical values by use of the Lovibond Tintometer. He noted that proper scouring prior to dyeing markedly improved crocking. Steward's instrument is well adapted to controlled crock tests on yarns, but is limited by the relatively large sample size of continuous yarn required to wind on the drum. Knots obviously would cause difficulties, especially with coarser yarns.

Forster, Ramachandran and Venkataraman (*14*) modified a Kleinewefers

yarn-mercerizing machine in 1938 for testing crock-fastness of naphthol dyes. The dyed yarn was stretched over the two rollers of the machine and a curved shoe covered with a piece of white cloth was held against the yarn on one of the rollers. The yarn was caused to rub against the white cloth by rotating the rollers. Test results were evaluated visually and also by laborious nitrogen-content determinations to obtain quantitative data on the amount of dyestuff removed. This test method again assumes the presence of sufficient sample size of continuous yarn to permit proper winding.

Derrett-Smith and Bradley (*15*) developed an instrument in 1940, which employs a bleached white strip of linen cloth clamped over a flat aluminum platform with a fixed clamp at one end and a detachable clamp at the other end attached to the overhanging end of the white cloth. The dyed material to be tested is wrapped around specially constructed wooden blocks, which in turn are attached to a light metal carriage. A heart-shaped cam, driven by a geared electric motor attached to the metal frame by connecting rods, provides a reciprocating motion. The wooden blocks carry detachable weights to insure close contact with the white cloth. Several tests may be run simultaneously. A special block was used for testing yarns which were wrapped around the block. The authors *varied the number of rubs to obtain a definite crock,* employing the concept expressed by Bean and Rowe. Sample size of continuous yarn appears to be less critical than with other test methods, but is still a limiting factor.

Martindale (*16*) developed a wear tester in 1942, which employs a circular abradent holder run in an elliptical rubbing pattern. Crock fastness is determined with this instrument by placing the dyed cloth on the table and rubbing with a piece of standard white calico inserted in the circular abradent holder. The color rubs off onto the white disc. The instrument appears to be impractical for yarn testing due to yarn movement under the elliptical rubbing action. This instrument is employed by Imperial Chemical Industries (*17*) to determine crock fastness. ICI claims that rubbing is more dependent upon the application method than the specific dyestuff, which has been borne out by the work of Millson, et al.

The Swiss Standards Association (*11*) and the International Organization for Standardization (*12*) specify the crockmeter for rubbing tests, but offer no suggestions on the application of the instrument for yarn testing.

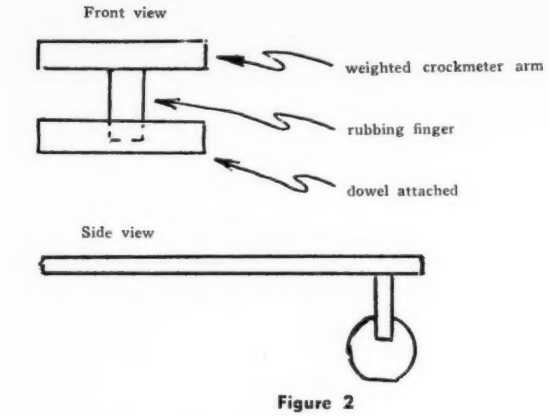

Figure 2

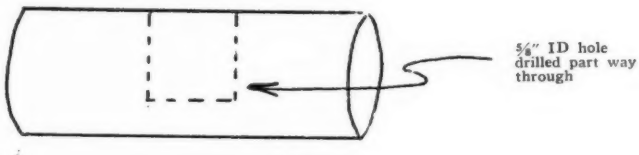

Figure 1

EXPERIMENTAL

Extensive use of the crockmeter in its standard form in our laboratory forcibly brought home its inherent design weaknesses for use in testing the six- to eight-inch yarn samples provided by our package and skein dyers for running quality control acceptance tests. Fine denier filament yarns proved to be particularly difficult to test.

A close observation of the crockmeter test on yarns revealed that the dowel finger was pushing the yarns aside, or sliding off them, rather than riding over them. The idea that a less blunt rubbing surface might ride over the yarns without pushing them aside was investigated. A wooden dowel of greater diameter than the 5/8" diameter rubbing finger was cut to a 2-inch length, and a 5/8" diameter hole was drilled *almost* through it as shown in Figure 1. This dowel was then inserted over the end of the crockmeter rubbing finger and set at right angles to the rubbing direction as shown in Figure 2. The crockmeter was then run for a protracted number of cycles against fine sandpaper to produce a flat surface on the bottom of the dowel, as shown in Figure 3, and grooves were cut at each end of the dowel to permit standard white crock cloth squares to be attached to the dowel by rubber bands at each end. The rubber bands were prevented from touching the yarn or the platform by being recessed into the grooves of the dowel, as shown in Figure 3. The exact dimensions of the dowel are shown in Figure 4. It was also found advisable to cover the abrasive paper on the crockmeter platform with a cardboard rectangle held in place over the emery paper with scotch tape on the four corners. The yarn to be tested is simply scotch-taped to the wooden area at each end of the cardboard-covered emery paper (the yarn should be drawn taut and aligned as nearly parallel as possible), and the white test square attached to the dowel in a smooth, wrinkle-free position. The crockmeter is then run for the desired number of cycles in the conventional manner. The pattern of crocking on the test square is rectangular, instead of round, and it is felt that the pattern represents an improvement over the conventional round spots because of the complete absence of bunching at the edges, as is commonly encountered with the dowel-end standard finger method. The rubber bands used should be as small as possible to permit a tight binding of the white square to the dowel.

RESULTS

Continuous use of the above method for the past few months has demonstrated that consistent results, fully correlated with the standard method, are readily obtained both wet and dry in much less time with less damage to the test yarn, and imperfect test patterns due to the finger moving

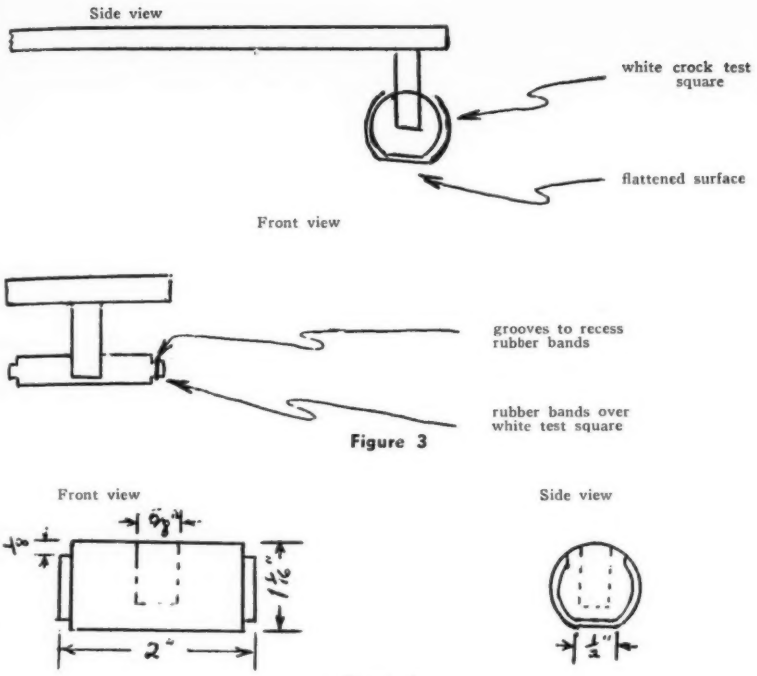

Figure 3

Figure 4

the yarns apart are no longer encountered. This modification has the advantage of utilizing a standard instrument and standard white test squares to produce results fully equivalent to the original method in less time and with greater consistency. It should also be noted that the standard instrument is not permanently altered in any way. The removal of the dowel attachment and the cardboard covering the emery paper is quickly performed, and the instrument is then ready for use on fabrics, with none of its effectiveness impaired, if the dowel attachment has been carefully applied to the crockmeter finger.

ACKNOWLEDGMENT

I should like to express my gratitude to the personnel of Boris Kroll Fabrics, Inc. for their cooperation and encouragement in the publication of this paper. A special debt is owed to Nicholas Di Iorio for his many suggestions and his fabrication of several variations of the dowel to determine the simplest and most effective size and shape.

LITERATURE CITED

(1) Durfee, W C, "The Rubbing Test", *Am Dyestuff Reptr* **35**, 591-2 (1946).
(2) Anon, "The Durfee Crock Testing and Recording Machine", *ibid* **25**, No. 10, 263 (1936).
(3) "Fastness to Crocking" *AATCC Year Book*, 129-32 (1935-1936).
(4) "Fastness to Crocking" *AATCC Year Book*, 176-81 (1937).
(5) Durfee, W C, "Some Features of Crock Tests", *Am Dyestuff Reptr* **26**, No. 15, 446-7 (1937).
(6) Millson, H E, Watkins, W H, and Royer, G L, "Studies on Wool Dyeing: Crocking", *ibid* **36**, No. 3, 45-63, 69-70, 122 (1947); *Calco Tech Bull* 780; *Textile World* **98**, No. 5, 127, 238, 242 (1948).
(7) "Crockmeters and Crockmeter Cloth—Revised Prices" *Am Dyestuff Reptr* **36**, No. 14, 392 (1947).
(8) New York Section, AATCC, "A Study of Factors which Influence the Fastness to Crocking", *ibid* **44**, No. 2, 34-40 (1955).
(9) "Fastness to Rubbing (Crocking) Tentative Method" *AATCC Year Book*, 192-5 (1944).
(10) Bean, P, and Rowe, F M, "The Effects of Aftertreatments on the Degree of Aggregation, Location, Shade and Fastness Properties of Insoluble Azo Colours on the Fibre", *J Soc Dyers Col* **25**, No. 3, 67-77 (1929).
(11) Swiss Union for Testing Technological Materials, Swiss Standards Association, "Textiles: Textile Testing Methods", *Am Dyestuff Reptr* **41**, No. 22, 701-27 (1952).
(12) Appel, W D, "Tests for Colorfastness of Textiles under Consideration in the International Organization for Standardization", *ibid* **42**, No. 26, 871-87 (1953); "Draft ISO Proposal on Methods for Testing Colorfastness of Textiles", *ibid* **45**, No. 6, 150-67 (1956).
(13) Steward, C O M, "A Machine for Testing Fastness to Rubbing", *Dyer* **73**, No. 11, 499-500 (May 24, 1935).
(14) Forster, R B, Ramachandran, S R, and Venkataraman, K, "Studies in the Naphthol AS Series. Part II—Fastness to Rubbing", *J Soc Dyers Col* **54**, No. 5, 216-55 (May 1938).
(15) Derrett-Smith, D A, and Bradley, H B, "A Machine for Testing the Fastness to Rubbing of Dyed Materials", *ibid* **56**, No. 6, 261-5 (June 1940).
(16) Martindale, J G, "A New Design of Cloth Wearing Tester" *J Textile Inst* **33**, No. 9, 151-8 (September 1942).
(17) Anon, "Fastness Assessment of Textile Dyestuffs" Imperial Chemical Industries Ltd, London, p 25.
(18) Anon, *Interchem Rev* 12, No. 4, 107, Winter 1953-4.

Abstracts

Solvent-Soluble Dyes Cause of Fading (in Drycleaning)

Bayley, C H and Tweedie, A S, *Can Textile J* 73, 57, February 10, 1956.

With the trend toward more drycleaning of cotton and other summer dresses in the past few years, cleaners have become increasingly aware of the problem of fabrics which fade or change shade uniformly in drycleaning, even in the absence of moisture. Some of these have been solid shades, others have had printed designs. Most of them were cotton fabrics, but some were made from other fibers, eg, some printed acetate fabrics. In multicolor prints, often only one or two colors were affected.

The dyes most commonly affected by drycleaning solvents are vat dyes and azoic dyes. These two classes of dyes are widely used on cotton fabrics because of their generally excellent fastness to washing and to light. Unfortunately, it has recently been found that certain individual dyes in these two classes will dissolve in organic solvents such as cleaning solvents. They are more soluble in perchlorethylene than in Stoddard solvent. The degree of dye loss is also increased by higher solvent temperatures.

Reds and pinks are the shades most frequently affected. A change of shade may occur if a combination of two or more dyes is used, and one of them is solvent-soluble.

This problem of solvent-soluble dyes does not appear to have been widely publicized as yet in the dyestuff literature. Public demand for fabrics that are color-fast to drycleaning will make garment manufacturers and fabric dyers and printers more aware of the need to select dyes which will not be dissolved out of fabrics by cleaning solvents.—WHC

Textiles with New Properties from Cellulose Triacetate (Arnel)

Stoll, R G, *Textile Research J* **25**, 650-61, July, 1955.

This paper outlines why cellulose triacetate, which has been known for 90 years, only recently became a fiber-forming material of considerable commercial interest. After giving a brief historical background, it describes the structure of triacetate as developed by heat treatment, and the utilization of heat treatment for the improvement of fiber and fabric properties. It further presents data on the durability of triacetate yarns and fabrics when exposed to various service conditions, and outlines the possible use in so-called "ease-of-care" and "wash-and-wear" fabrics and garments.

The author points out that the most important trend in apparel textiles at the present time, and probably in the future, is the development of these "ease-of-care" and "wash-and-wear" fabrics. This development was made possible by the introduction of the hydrophobic and thermoplastic synthetic fibers upon which water has little or no effect and which can be heat-set so that the geometry given by the yarn and fabric structure becomes the natural configuration of the fibers. Triacetate also offers the possibility of developing fabrics which will retain their original shape, texture and appearance even when exposed to high humidity or washing and drying.

Regarding dye affinity, when dyed under the typical conditions for dyeing secondary acetate, the dyeing rate of Arnel triacetate is considerably lower. However, by the use of higher dyeing temperatures and certain dyeing assistants (eg, tripropyl phosphate), it is possible to obtain a dyeing rate comparable to that of regular acetate. The selection of the most suitable dyes is important.

The author reminds us that since the stretching and shrinkage behavior of triacetate fabrics in slashing, weaving, scouring, dyeing, and heat treatment is different from that of existing fabrics, the loom constructions which were developed for rayon, acetate/rayon and other man-made and natural fibers must be modified.—WHC

A New Approach to the Continuous Dyeing of Cellulose Fabrics with Direct Cotton Dyes

Wegmann, J, *J Soc Dyers Colourists* **71**, 777-89, December, 1955.

There are two main reasons why direct cotton dyes are difficult to apply by continuous methods. First, it is difficult to maintain uniformity of color during the dyeing process because of the affinity of the dye for the fiber. Second, direct cotton dyes of good wet fastness have a low rate of diffusion, which means that a longer steaming time is necessary to bring about fixation.

It has been found that copper-complex polyazo dyes form loose complexes with certain amines, and that these complexes diffuse rapidly and can be applied evenly to the fiber. These amines are displaced during steam fixation in an ager and are subsequently removed by rinsing, which results in a normal dyeing .

From the application point of view, the problem has been to manufacture amine complexes of copper-containing direct dyes which are stable enough not to hydrolyze in aqueous solution, especially at elevated temperatures, but yet are not so firmly united as to prevent the cellulose fiber from displacing the amine base to permit adsorption of the dye molecule. Several amines, particularly those containing hydroxyl and carboxyl groups, were found by the author to meet these requirements.

He states that the amine complex of a copper-complex dye has dyeing properties differing considerably from those of the same dye applied without the amine. The depth of color, at a given temperature and with a given concentration of electrolyte, is reached very rapidly. The properties of the dyed color remain the same whether the dyeing is carried out with or without the amine.

The author states that this method permits simple and reliable continuous application of highly substantive direct dyes, such as are to be found in the range of copper-complex products.

Twenty-five references to the literature are cited.—WHC

Bleaching of Nylon and Nylon Blends

Shaw, S and Willson, W S, *J Soc Dyers Colourists* **71**, 857-71, December, 1955.

The effect of chemical bleaching agents on the strength and color of all-nylon textiles, and on the tensile strength and abrasion resistance of wool-nylon, cotton-nylon, and staple viscose rayon-nylon blended fabrics has been investigated. In addition, methods of bleaching a cotton-nylon blended fabric to give an acceptable white is described. Removal of heat-setting discoloration from all-nylon material is discussed, and also the use and misuse of fluorescent brightening agents. The bleaching agents selected for investigation were sodium hypochlorite, hydrogen peroxide, peracetic acid, and sodium chlorite, and details are given of recommended methods of application.

The conclusions reached by the authors on the relative merits of the four bleaching agents may be summarized as follows:

ON ALL-NYLON———Sodium hypochlorite has no bleaching action.

Hydrogen peroxide has a slight bleaching action, but alkaline liquors cause severe degradation of the fiber. Acid liquors cause relatively slight degradation.

Peracetic acid has a bleaching action, removes heat-setting discoloration, and can be used when certain colored effect threads are present. There is some loss in tensile strength, which should not exceed 10 percent.

Sodium chlorite has a bleaching action, removes heat-setting discoloration, but generally cannot be used in presence of colored effect threads because of its stripping action. There is little or no degradation of the fiber.

ON WOOL-NYLON BLENDS——Blends containing up to 25 percent nylon can probably be bleached safely with peroxide by the normal alkaline methods used for wool (this requires bulk confirmation). For blends containing a large percentage of nylon, the acid methods are safer.

ON COTTON-NYLON BLENDS———To obtain an acceptable white, a combined scour and peroxide bleach may be used, or a hypochlorite bleach aftertreated with peracetic acid or acid sodium chlorite.

The authors furnish 21 references to the literature.—WHC

Some Aspects of Present-day Bleaching Practice

Crowder, N F and White, W A S, *J Soc Dyers Colourists* **71**, 764-76, December, 1955.

This paper is a general review of modern practices and developments in the bleaching of various textiles, the emphasis being mainly on cotton. Continuous bleaching processes and the use of sodium chlorite are particularly mentioned.

Cotton. The main bleaching agents used in commercial practice are sodium and calcium hypochlorite, hydrogen and sodium peroxide, and sodium chlorite. The preliminary operations (desizing, kier-boiling, etc.) are briefly discussed. The peroxide bleach has the advantage over hypochlorite in that it is capable of combining scouring and bleaching in one continuous operation. The author describes several different continuous bleaching ranges, including the Du Pont (peroxide), Becco (peroxide), and Mathieson (peroxide or

chlorite) systems. They point to the spectacular developments in the continuous process, particularly in the U.S., but state that in Britain the conventional process has remained in favor because on the whole it gives a higher standard of bleaching and is more easily adapted to the processing of a wide variety of cloths in comparatively small quantities.

The advantages of the sodium chlorite process are described (eg, little or no tendency to degrade the cellulose). Its disadvantages are its corrosive action on metals and the liberation of chlorine dioxide fumes.

Linen. The modern bleaching process for yarns, according to the authors, consists of a mild scour with soda ash and a neutral or acidified hypochlorite bleach, followed by a peroxide steep. For cloth, to obtain the best white, they recommend a lime-sour-soda ash sequence, followed by alkaline hypochlorite and souring.

Sodium chlorite also has much merit as a bleach for linen. A three-stage process is recommended: mild scour-chlorite-peroxide; this is said to give a good white with low weight loss.

Jute. Either hypochlorite or peroxide may be used, several formulas are suggested. Jute bleaching is carried on only to a limited extent.

Rayon. Viscose fibers are usually bleached during manufacture. For very good whites the fabrics may be further bleached with either hypochlorite or peroxide. Mixtures of rayon and cotton require particular care, as the rayon may be tendered by the more thorough treatment required for the cotton.

Wool. This was formerly bleached by the sulfur stoving process, but this has now been largely superseded by peroxide, which gives a better white. The peroxide bleach is described in detail.

Synthetic Fibers. Nylon is usually bleached with sodium chlorite, according to the authors, but peroxide and peracetic acid may also be used. Hypochlorite has no action on nylon. Polyester fibers may be bleached with chlorite, acidified with nitric acid. Acrylic fibers can be bleached with oxalic acid; alkaline agents turn the fiber yellow.

The paper closes with 43 references to the literature.—WHC

A Compounded Flame Retardant for Cotton Fabrics

Reid, J D, Frick, J G Jr, and Arceneaux, R L, *Textile Research J* **26**, 137-40, February, 1956.

Two finishes had been previously developed in the Southern Regional Research Laboratory as flame retardants for cotton fabrics: the "THPC" method, based on a copolymer made from tetrakis (hydroxymethyl) phosphonium chloride and methanolmelamine, and the "BAP" method, using a polymer prepared from bromoform and triallyl phosphate. Both methods give good resistance to burning, as judged by the vertical flame test, but for some uses, particularly to meet military requirements, it was considered desirable for the fabric to withstand a more rigorous test.

It was found that a combination of the two methods (THPC and BAP) will produce a flame-retardant finish for cotton that is superior to either finish applied separately, and imparts a high degree of flame resistance to 8 oz or heavier fabrics. A good, but somewhat lower degree of resistance is obtained on fabrics of lighter weight.

The application of the new combination method is simple, consisting of impregnation on a padder, drying, curing for 5 minutes at 140° C in a vented oven, followed by washing and drying. The preparation of the impregnating liquor containing the two components is described.

The durability to repeated laundering of this flame-retardant finish, particularly on the heavier fabrics, is said to be good. The treatment has some adverse effect on the tear resistance of the fabric, to an extent dependent on the type of cloth used. A twill fabric was practically unaffected.

The theoretical aspects of making cotton flame-resistant are discussed.—WHC

The Effect of Chlorine and Subsequent Treatment with Sodium Bisulfite upon the Physical Properties of Cotton Fabrics Treated with Various Resins

Howard, J H, *Textile Research J* **26**, 124-8, February, 1956.

A study has been made of the effect of chlorine on the tensile strength, tear strength, and crease resistance of mercerized 80x80 white cotton cloth treated with three types of thermosetting resins, one of which was a straight urea-formaldehyde type (UF), another belonged to the melamine-formaldehyde group (MF), and the third was of the imidazolidone-formaldehyde class (IF).

The fabric was padded with the three resins, dried, and cured for 2 minutes at 350°F. Samples were then saturated with a solution of 0.25% available chlorine, washed well in water, and dried. Scorch tests were also made. Other samples of the resinated cloths were treated with sodium bisulfite. Still other samples were treated with chlorine, followed by bisulfite.

All samples were compared for tensile and tear strength and wrinkle resistance, and also for color change. The results are given in tabular form.

The tests show that the IF resin is the least chlorine-retentive of the three. The other two resins are extremely chlorine-retentive.

Chlorine treatment of the UF finish causes a material loss in wrinkle recovery; the same treatment on the MF finish has little effect.

The IF finish gives the highest wrinkle recovery, but the lowest tensile strength of all.—WHC

Dyeing Triacetate with Disperse Dyes

Eisele, J and Federkiel, W, *Textilber* **36**, 1036-41, October, 1955. (Translated by P J Wood)

Triacetate, which is now being produced on a commercial scale, is stated to have a number of advantages as a fiber over secondary acetate, including a higher melting point; better resistance to ironing; greater wet strength; more resistance to saponification; and better heat-stabilization properties. It does not lose its luster in a boiling dyebath.

Disperse dyes display the same mechanism of dye absorption and diffusion on both fibers. Although equilibrium between dyestuff in the bath and on the fiber is reached more slowly with many dyes on triacetate, the fiber has at least an equal or even greater capacity for dyes than secondary acetate.

The best temperature for dyeing triacetate is said to be 95-100°C, but dyeing under pressure up to 125-130°C greatly accelerates the rate of diffusion, and permits heavy shades to be dyed in less than an hour.

The fastness of dyes on triacetate to water, perspiration, washing and fulling is better than that on secondary acetate, according to the authors. The lightfastness on the two fibers is about the same. Triacetate may be drycleaned successfully with perchlorethylene.

For dimensional stabilization a heat treatment of 5 seconds at 220°C is recommended for triacetate fabrics. Dyes that sublime at this temperature must not be used.

The fastness to atmospheric gas fading is about the same on both fibers. It is pointed out that GFN-Inhibitor (BASF) loses its effectiveness when applied at 95-100°C on triacetate that has been heat-stabilized. A temperature of 85°C or lower is recommended.

Carriers have varying effects with different disperse dyes on triacetate. In general, those that are most effective on Dacron are also effective on triacetate.—WHC

THE ESTIMATION OF COPPER-8-QUINOLINOLATE IN MILDEWPROOFED FABRICS*

Arthur Rose, A Witt Hutchison, John R Hayes, and Irene R Sharkey
Applied Science Laboratories, Inc, State College, Pa

A method for the estimation of copper-8-quinolinolate in fabrics which have been treated with this fungitoxic agent is described.

The method is based on the photometric determination at 410 mμ of the copper-8-quinolinolate in chloroform solution. In the recommended procedure the fungicide is removed from the fabric by boiling the sample in dilute sulfuric acid for a short time. After adjusting the pH of this solution to about 6, the copper-8-quinolinolate is extracted with chloroform.

Other copper-containing fungicides such as copper naphthenate and copper hydroxy naphthenate do not interfere, nor do substances ordinarily employed to render fabrics water- and fire-resistant.

INTRODUCTION

THE widespread use of copper-8-quinolinolate in mildewproofing cotton indicated the desirability of having a simple and rapid procedure for the estimation of this fungitoxic agent on treated fabrics. Since formulations frequently make use of copper-8-quinolinolate in conjunction with other copper-bearing toxic agents, such as copper naphthenate and copper hydroxy napthenate, methods based upon the determination of total copper in the sample are not applicable. Further, to be generally useful, the method should be one which will give accurate results in the presence of other agents which may have been applied in the treatment of the fabric to render it fire, weather, and water resistant.

Shortly after the completion of the work to be described, Darbey (*1*) published the results of his investigations on the determination of copper-8-quinolinolate in cotton textiles. The method developed was based on the determination of the concentration of 8-hydroxyquinolinium ion in the solutions resulting from the extraction of fabric samples with hot dilute hydrochloric acid by measurements of their absorbencies at 365 mμ. The method was recommended as being applicable to samples in which seriously interfering substances are known to be absent and in which the copper-8-quinolinolate is soluble in the hot hydrochloric acid. Darbey stated that samples dyed with "mineral khaki" may not be studied by the method, because of the interference of ferric chloride in the light absorption measurements.

In the present work a method has been developed which satisfactorily meets the requirements of typical FWWMR fabrics. It is based upon a photometric determination of copper-8-quinolinolate in chloroform solution. The copper-8-quinolinolate is removed from the fabric by boiling dilute sulfuric acid and, after adjusting the pH of this solution to about 6, is extracted with chloroform.

The spectrophotometric properties of solutions of copper-8-quinolinolate have been described by Moeller (*2*) in connection with a study of a method for the separation of copper from other metals making use of the extraction of aqueous solutions at controlled pH values with chloroform containing 8-hydroxyquinoline. He reported that solutions of copper-8-quinolinolate in chloroform exhibit a maximum absorbence of light at 410 mμ and that dilute solutions obey Beer's law. These findings have been confirmed in the present study.

The nature of the absorbence curve for a chloroform solution of copper-8-quinolinolate is shown in Figure 1 in which the transmittancy values have been plotted against the wave length. The data were obtained with a Beckman DU spectrophotometer.

In the preliminary studies measurements of the transmission of light at 410 mμ of various solutions of copper-8-quinolinolate in chloroform were made with a Beckman DU spectrophotometer, a Bausch and Lomb monochromatic colorimeter and a Fisher Electrophotometer. All yielded data which showed that the measurement of light absorption could be used to determine the concentration of the compound in the solutions. The Fisher Electrophotometer was utilized in the studies of the fabric samples and the transmission curve as obtained with this instrument equipped with a 410 mμ filter is shown in Figure 2. Micro cells approximately 1 cm in diameter were used in obtaining these data and in the fabric analyses.

PROCEDURE

Prepare a representative sample of the fabric by cutting selected portions into squares approximately ¼" on a side and mixing these thoroughly. To a one-gram portion of the sample, weighed to the nearest milligram, add 20 ml of 10% sulfuric acid and heat the mixture to the boiling point. It is important to limit the sample to 1 gram, and the boiling should not be prolonged, in order to avoid difficulty in filtering and other subsequent operations. Filter at once through No 40 Whatman paper. Transfer the filter paper and contents back to the original beaker or flask, and add 10 ml of 10% sulfuric acid. Again heat to boiling and filter. Repeat a third time with another 10 ml portion of the sulfuric acid. Wash the paper and contents three times with 5 to 10 ml portions of hot water. Combine all the sulfuric acid extracts and hot water washings.

Adjust the pH of the solution to about 6.0 by the addition of dilute (1-1) NH_4OH. This adjustment need not be precise—pH values from 5 to 7 will permit quantitative extraction of the Cu-8 by chloroform. Transfer the solution quantitatively to a 500 ml separatory funnel. Shake with several small (10-15 ml) portions of purified $CHCl_3$. Continue the extractions until all yellow color has been removed, as shown by the lack of any color in the chloroform layer. Combine the chloroform extracts. To the combined extracts add 5 to 10 g of pure anhydrous sodium sulfate. Stir and let stand a few minutes in order to remove water from the chloroform solution. Transfer carefully to a volumetric flask, and dilute to the mark with chloroform. In general, a 100-ml volumetric flask will be found convenient. If the amount of copper-8-quinolinolate is very small, it will be possible to extract all of it with less than 50 ml of chloroform, while if the content is high, it may be more convenient to dilute in a 250-ml flask. Determine

*Presented to the Deterioration Section, Society for Industrial Microbiology, AIBS Meeting, Madison, Wisconsin, September, 1953.

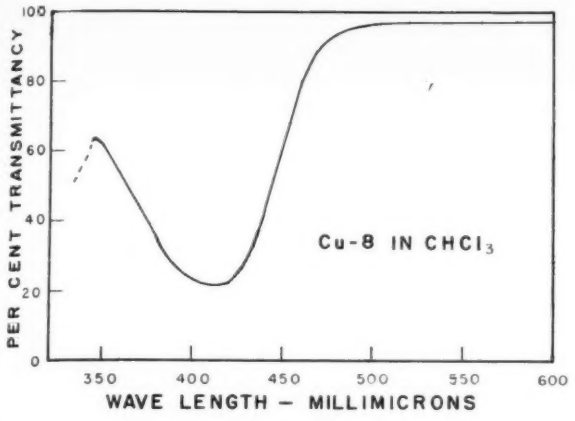

Figure 1
Light absorption by copper-8-quinolinolate in chloroform

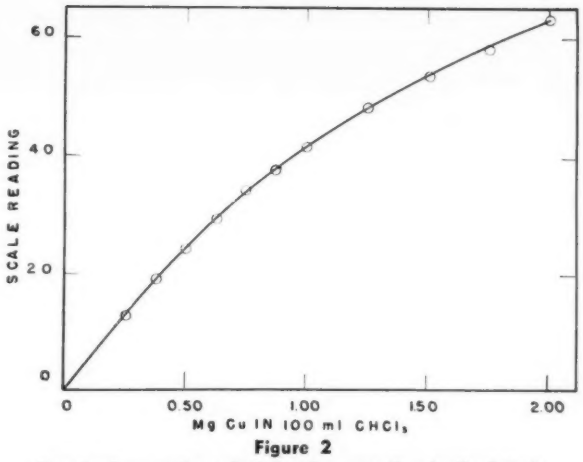

Figure 2
Standard curve for solutions of copper-8-quinolinolate in chloroform at 410 mμ with Fisher Electrophotometer

the percent transmission at 410 mμ by means of a spectrophotometer or equivalent instrument. Cells of 1-cm thickness are recommended. As the reference the chloroform extract from a sample which has been water-proofed, flame-proofed and dyed, but which contains no copper-8-quinolinolate may be used.

A standard curve is prepared by measuring transmissions of solutions of copper-8-quinolinolate in chloroform of known concentrations. These standard solutions may be made by dissolving the pure solid compound directly in the chloroform.

The weight of copper-8-quinolinolate in the sample is found by comparing the transmission value obtained with the standard curve.

RESULTS

Preliminary experiments showed that copper naphthenate solutions in chloroform had a negligible absorption of light at 410 mμ. Further it was shown that duck samples treated with fire, water and weather resistant formulations, but containing no fungicide or containing only copper naphthenate or copper hydroxy naphthenate, when carried through the above procedure yielded solutions with negligible light absorption at 410 mμ.

The fabric samples examined were fire, water, and weather resistant treated duck (U.S. Army Specification 6-345), for the most part of 12.24-oz. weight, in which various copper fungicides were incorporated in the treating bath. Sample A contained no added fungicide.

In a series of preliminary experiments known additions of copper-8-quinolinolate were made and the sulfuric acid extract carried through the procedure outlined above. The results which are given in Table I show that the added copper-8-quinolinolate is quantitatively recovered and that the components of the FWWR treatment do not interfere, nor do copper naphthenate and copper hydroxy naphthenate.

TABLE I
PRELIMINARY EXPERIMENTS

Sample		mg copper (as Cu-8) Added	Found
10% H_2SO_4		1.00	1.00
"		2.00	2.07
Fabric A		1.00	1.01
"		2.00	2.06
Fabric E		1.00	1.05
Fabric F		1.00	1.05
Fabric A	FWWR-treated—No fungicide		
Fabric E	FWWR-treated—contained 0.325% Cu as copper naphthenate according to treater's value based on pick up.		
Fabric F	FWWR-treated—contained 0.450% Cu as copper hydroxy naphthenate based on pick up.		

TABLE II
PHOTOMETRIC DETERMINATION OF COPPER-8-QUINOLINOLATE ON FWWR FABRIC

Fabric	Treater's Values (%Cu) Cu-N	Cu-OH-N	Cu-8	Cu-8 Found (%Cu) Average
A	0	0	0	0
B	0.286	0	0.047	0.042
C	0	0.335	0.042	0.040
D	0	0	0.168	0.150
E	0.325	0	0	0
F	0	0.405	0	0
I	0	0.43	0.017	0.007
J	0	0.43	0.05	0.039

Copper-8 applied as Quindex in B, C, and D, as Cunilate in I, and as Milmer in J.

TABLE III

Fabric	% Cu as Cu-8 ASL	PQD
M	0.008	—
	0.008	—
N	0.0047	0.005
	0.0047	0.004
O	0.013	0.010
	0.013	0.011
P	0.00	0.00
	0.00	0.00
Q	0.025	0.024
	0.024	0.027
		0.023
R	0.039	0.035
	0.039	0.038
		0.033

The results of analyses of samples in which copper-8-quinolinolate was added as a fungitoxic agent in the fabric treatment are given in Table II. The average value listed represents the average of 4 to 6 individual determinations in which the extreme variation was less than 10% of the value in general. The values are seen to be somewhat lower than those based upon the treater's estimate but this may not be significant.

In addition to those fabrics for which treater's values were available several additional fabrics were analyzed by the method. In each of these samples an analysis was made by the present procedure independently in the laboratories of the Philadelphia Quartermaster Depot. The results of these analyses are given in Table III.

DISCUSSION

From the results of the various experiments tabulated it is evident that the method yields reproducible results with samples of duck which has been FWWMR treated. The experiments in which known additions of copper-8-quinolinolate were made to sulfuric acid or to the sulfuric acid extract of fabric samples shows that the method gives accurate results also.

In the event that other metal quinolinolates were to be added to the fabric some interference might be expected. The presence of such substances seems unlikely, however,

and even if they were present, it is probable that any interference from them could be eliminated by close control of the pH of the aqueous solution prior to the chloroform extraction step.

SUMMARY

A method for the determination of copper-8-quinolinolate in FWWMR treated fabric based upon the photometric estimation of this substance in a chloroform solution has been developed. Substances normally present in such fabrics do not interfere.

ACKNOWLEDGEMENT

The authors are indebted to the Chemicals and Plastics Branch of the Research and Development Division of the Office to the Quartermaster General under whose auspices this work was carried out. (3) They are especially grateful to Drs Ray Treichler, Paul F Klens, Milton Manowitz, R E Vickland, and A M Kaplan for helpful discussions and suggestions during the period of time when this work was in progress.

REFERENCES

(1) Darbey, A, *Am Dyestuff Reptr* **42**, 453 (1953)
(2) Moeller, T, *Ind Eng Chem, Anal Ed*, 15, 346 (1943)
(3) Rose, Arthur, Hutchison, A W, and Hayes, J R, "The Estimation of Copper-8-quinolinolate in Mildewproofed Fabrics—Methods Applicable in Presence of Other Copper-Containing Fungicides," Final Report to Chemicals and Plastics Branch, Research and Development Division, Office of Quartermaster General, Washington, D C, Contract DA-44-109-qm-1239, 15 December 1953.

• PATENT DIGEST •

PAUL WENGRAF

COPPER COMPLEX SOLUTIONS OF NATURAL SILK——Aftertreatment with Alcoholic Acids

G,2,01

USPat 2,733,975 (Whitner——Feb 7, 1956)

Several patents granted to the same inventor are based on the use in textile applications of solutions containing natural silk fibers in alkanolamine copper complexes (see references below). The dispersed silk substance is then precipitated by a treatment with acidic agents, followed by rinsing, to remove residual copper and alkanolamine salts.

The current patent refers particularly to the acid-treating step. It has been observed that a smoother and fuller feel can be imparted to the fabric by an aftertreatment with a *predominantly alcoholic acid*, for instance, with hydrochloric acid in 85% isopropanol, instead of the usual hydrochloric acid acid rinse in aqueous medium. Thus the composition used for dispersing silk fiber (waste) may contain the blue complex obtained from cuprichloride and diethanolamine plus alkali. Upon being acidified with the alcoholic hydrochloric acid solution, the silk is precipitated on the fiber. The hydrochlorides of diethanolamine and copper that are formed are soluble in the alcoholic solution. Alkalichloride generated in this process is insoluble in alcohol and has to be removed separately in another rinse with water). The finished goods eventually contain silk fiber substance as a weight-increasing agent, all the other residues having been rinsed out.

References cited by the Patent Office:

USPat 2,565,832 / 1951 [cf *Am Dyestuff Reptr* 40, 826 (1951)], USPat 2,446,682 / 1948 [cf *Am Dyestuff Reptr* 38, 109 (1949)], and USPats 2,417,-388-9, granted to the same inventor, refer to dispersions of silk in alkanolamine-copper complexes in alkaline media, to compositions containing very small amounts of free alkali, or to compositions wherein tetra alkyl ammonium hydroxide replaces alkali and acts simultaneously as a complex-forming compound.

USPat 1,936,753 (Celanese Corp of Am 1933): dissolving natural silk waste in phosphoric or sulfuric acids and spinning into a cold coagulant, eg, ethanol.

USPat 1,955,221 (I G Farben A G / 1934): dissolving fibroin in copper-oxide ammonia complex while maintaining the temperature below 0°C.

VAT DYEING NYLON—— Pretreatment with Phthalic Anhydride in Phenol Solution

C,4,07

USPat 2,693,994 (General Aniline & Film Corp ——Mautner——Nov 9, 1954)

The vat dyeing of nylon requires elevated temperatures (up to 200°F) to obtain a full shade, but the light fastness of these shades was found to be poor as compared with analogous dyeings on cellulosic material. A tannic acid pretreatment, advocated in prior references, gives satisfactory deep colors, but light or medium shades discolor, especially upon alkaline washing.

This invention comprises a preliminary treatment with a 2-5% solution of phthalic anhydride in phenol. Phenol per se, frequently used as a swelling agent for nylon, has highly toxic and skin-irritant properties, making handling of the goods difficult. It also has a strong solubilizing effect on the fibers, thus requiring strictly controlled working conditions. In contrast, the phenolic solution containing phthalic anhydride reportedly avoids these disadvantages substantially. Vat dyeings carried out on material thus prepared are found to be equal and in some instances superior to those obtained on cellulosic fibers. A reaction may take place between phenol and anhydride. The aqueous solution was found to be rather unstable under atmospheric conditions where phthalic acid slowly settles out. But even in this event the effect is noticeable unless the content of phthalic anhydride drops below about 2%. This treatment is carried out at 150-210°F with aqueous solutions of 1-2.75% concentration on solids.

Example: a nylon skein was pretreated for 5 minutes at 200°F in a solution of 200 ml water, containing 5 ml of a solution of 5% phthalic anhydride in phenol. Thereafter the material was rinsed in cold water, dyed in an alkaline hydrosulfite containing vat of Indanthrene Brown RN Double Paste (*C I* 1151), reoxidized and scoured as usual.

Other examples refer to dyeing with various vat dyes (Indanthrene Dark Blue PO, Indanthrene Golden Orange G, etc) or with dimethoxy violanthrone or the dye reported in Schultz' "Farbstofftabellen" #1269, that is, dimethoxy dehydro dibenzanthrone or Indanthrene Brilliant Green B.

References cited by the Patent Office:

Brit Pat 645,033 (Imperial Chemical Industries/1950): nylon solvents characterized by 5 atoms linked together

(Concluded on page 389)

THE HIGH-TEMPERATURE DYEOMETER: An Instrument for Studying Color Reactions at Elevated Temperatures

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The High-Temperature Dyeometer has been found useful in the study of many reactions at different temperatures but is particularly adapted for obtaining quantitative dyeing data at higher temperatures, ie, 212°F to 300°F.

Examples are described showing its application to measurements at temperatures above the boil, of 1) rates of chromation, 2) rates of decomposition of dyes and 3) rates of exhaustion of different kinds of dyes on different kinds of fibers.

INTRODUCTION

THE dyeing of textile fibers at high temperatures (above 212°F) has received considerable attention during the last few years. This is due in part to the increased use of the hydrophobic fibers. The rates of diffusion of dyes into the hydrophobic fibers are apt to be especially slow, and, as a result, it is extremely difficult to obtain satisfactory penetration in any normal dyeing process with these fibers. For example, Waters (*1*) found that the rates of diffusion of disperse dyes in Terylene are almost 500 times slower than in cellulose acetate. For that reason Terylene presents a difficult problem although the fiber possesses a sufficient number of sites of the ester type for the absorption of the disperse dyes, and heavy shades are possible if the dye can be gotten inside the fiber. The increase in diffusion rate is the biggest single advantage gained by high-temperature methods. However, there are additional advantages since, as the temperature is raised, dyes generally become much less aggregated and the fiber structure less compact and rigid due to the increased thermal agitation.

Practical methods for employing high temperatures are well known today. Special package and stock dyeing machines, pressure jigs, the Burlington machine and the Barotor are examples of some of the closed machines which operate under pressure at high dyeing temperatures. All of these operate by batch processing methods. Only one commercial continuous-pressure dyeing machine has received public attention. This is the Uxbridge high-temperature continuous dyeing machine, which has made it possible to dye wool fabric continuously at 25 yards per minute (*2*) at temperatures up to 275°F. An extreme example of the use of higher temperatures, in which no pressure is involved, is the Thermosol Process. In this process a fabric, on which a suitable dye has been padded and dried, is exposed for several seconds to very high temperature, as high as 400° to 425°F.

Various types of laboratory dyeing equipment have been used by different investigators in the study of high temperature dyeing. In work done by the Philadelphia Section of the AATCC (*3*) a so-called Tube machine was used. In this apparatus, glass pressure tubes containing the fiber and dye liquor, and enclosed in a metal shield, were rotated end over end in a glycerine bath held at the desired temperature. At the conclusion of the dyeing cycle, the tubes were removed from the glycerine bath and cooled by being held under running water. When studying high-temperature dyeing, many laboratories have made use of a laboratory package-dyeing machine, which is specially designed for operating under pressure. A disadvantage of this method, and also of the Tube machine described above, is that the material to be dyed is in contact with the dyebath while the bath is being heated to the higher temperature. Under such conditions the behavior at one temperature cannot be observed. For example, quantitative measurements of dyeing rates at high temperatures are quite impossible since some dye goes onto the fiber throughout the entire temperature range.

A small, laboratory noncontinuous dyeing unit (*4, 5*), which avoided this difficulty, was designed earlier in the laboratories of the American Cyanamid Company for dyeing at temperatures up to 300°F under 50 psi air pressure. In operation, the dye solution or developing bath was placed in a lower chamber. A platform valve, which separates this from an upper chamber, was pulled up into place against a seal, and held there by air pressure in the lower chamber. The material to be dyed was then placed in the upper chamber. When the dyebath had been heated to the desired temperature, air pressure was introduced into the upper chamber. This caused the platform-valve to drop, permitting the sample to fall into the dyebath. This apparatus was an improvement over the others mentioned in that no dyeing occurred until the bath reached the maximum temperature. But it was not adaptable to a continuous quantitative measurement of the dyebath concentration.

For any dyeing process to be studied effectively, it is important that the dyebath concentrations be known at all times. This could not be done with any of the previously described high-temperature dyeing equipment. The Dyeometer (*8*) developed in the Research Laboratories of the American Cyanamid Company provided a convenient method for getting a continuous record of dyebath strength. Many types of measurements have been made using the Dyeometer such as: 1) the rates of exhaustion, 2) stabilities of dyes, 3) rates of reduction of vat dyes and 4) rates of chromation. This equipment, however, could not be used for measurements above the boil. Since many of the newer fibers do not dye satisfactorily at temperatures below the boil, it was necessary that special equipment be designed for the study of the high-temperature-dyeing processes. For that purpose a new type of Dyeometer was built. The design and the operation of this High-Temperature Dyeometer will now be described.

APPARATUS

DESCRIPTION OF THE HIGH-TEMPERATURE DYEOMETER———Figure 1 is a photograph

NOTE: Calcozine, Calcochrome, Calcodur and Calcosyn are trademarks of American Cyanamid Co.

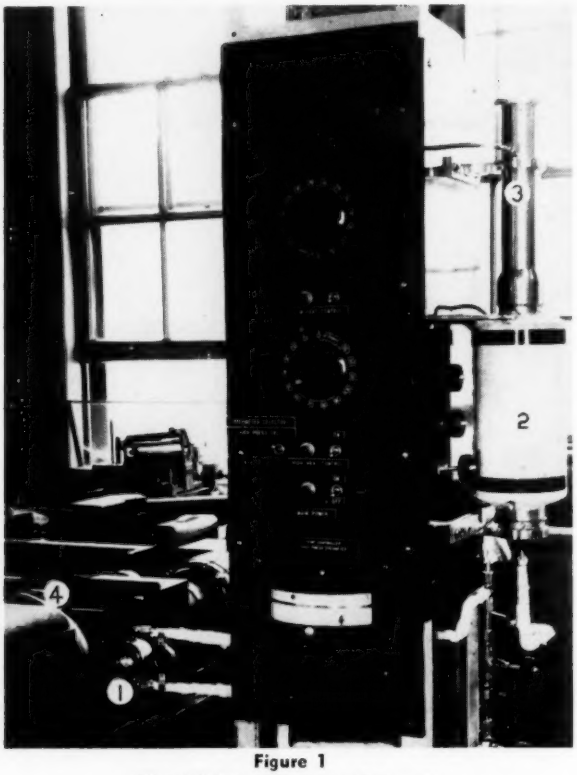

Figure 1
The High-temperature Dyeometer
1) 2-mm sample cell
2) Dyeometer kier—lower section
3) Dyeometer kier—upper section
4) GE-type recording spectrophotometer

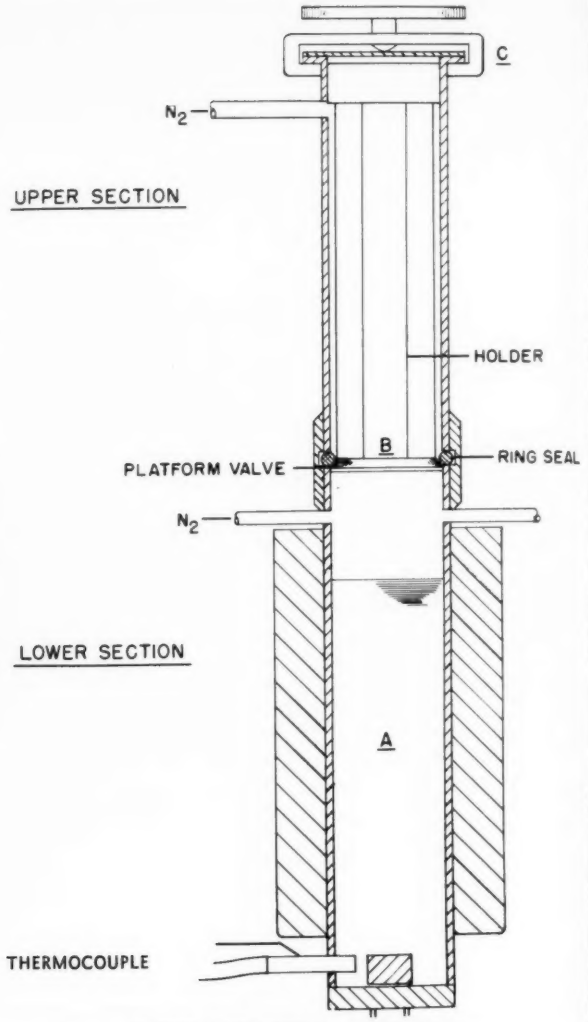

Figure 2
Cross section of the dye kier

of the High-Temperature Dyeometer unit. Figure 2 is a cross-sectional drawing of the dye kier. The capacity of the bath for proper circulation is 400 ml. As can be seen from the cross-sectional drawing, the vessel, like the earlier Cyanamid laboratory pressure dyer (*4*), consists of two sections. The dye solution or chemical bath is placed in the lower section, A, and is circulated by a motor-driven pump through a transmission cell, which is in the light beam of a recording spectrophotometer. A platform-valve, B, separates the two sections. At the beginning of a test this valve is pulled into place against a ring seal and held there by nitrogen pressure in the lower section. The dyebath is heated by electrical coils, which are wound around the lower half of the vessel. The sample to be dyed is mounted on a suitable holder and then placed on the platform valve, B. The cover seal, C, is fastened on the top of the vessel. When the desired temperature has been reached, nitrogen is let into the top section until the pressure in the upper section equals that in the lower.

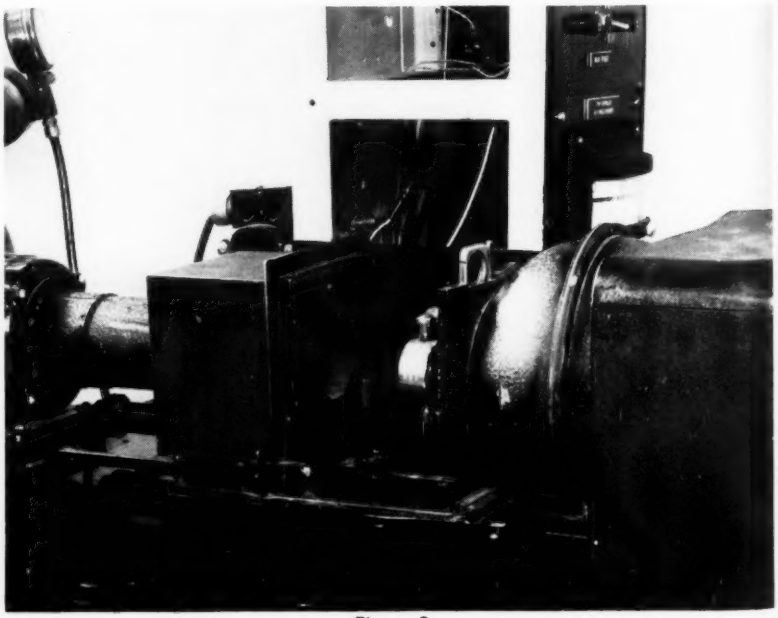

Figure 3
The cell of the High-Temperature Dyeometer being positioned in the sample beam of a spectrophotometer

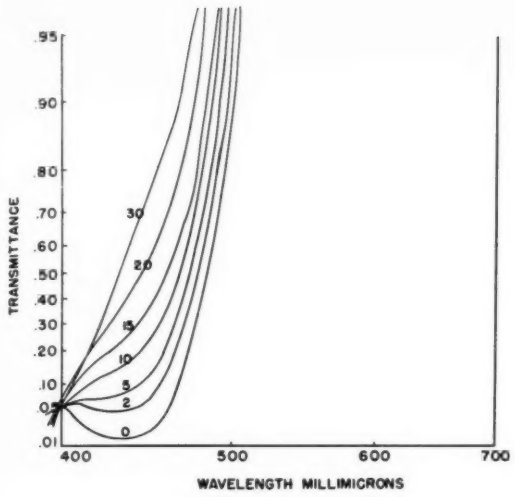

Figure 4

Stability of Calcozine Yellow OX at 250°F
Curves show the transmission after the time (in minutes) indicated

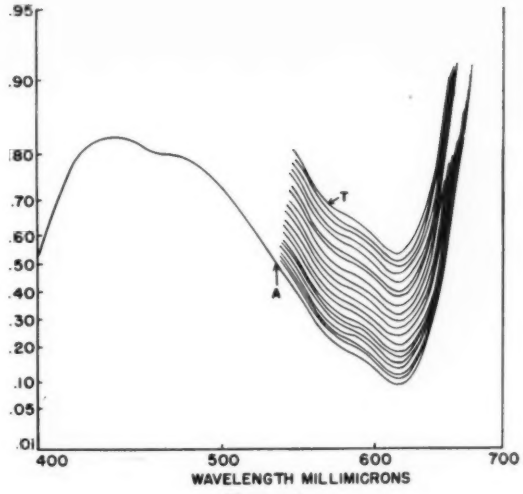

Figure 6

Exhaustion curves obtained during the dyeing of Vat Jade Green on Orlon 42 at 230°F for 90 minutes

The dyebath contained 0.15 g dye, 1 oz/gal $Na_2S_2O_4$, 2 oz/gal K_2CO_3 and 400 ml H_2O

When the pressure in the two sections is equal, the platform valve drops, permitting the sample to fall into the dyebath. At the end of the dyeing period, the dyebath can be blown immediately to the drain, or the temperature can be lowered gradually before the dyeing unit is drained.

The Dyeometer unit is so mounted that the transmission cell of the High-Temperature Dyeometer can be positioned in the sample beam of a GE recording spectrophotometer. Spectrophotometric measurements of the dye solution can be made continuously or at any desired time interval. Figure 3 is a photograph of the cell in the High-Temperature Dyeometer being positioned in the sample beam.

The Dyeometer can be used over a wide range of dye concentrations by employing several cell units of different cell thicknesses. A 1-mm cell and a 2-mm cell have been found adequate for a wide range of dyebath concentrations.

The heating rate is controlled by a variable transformer. The temperature is controlled automatically within ±1°F at any desired temperature setting by a pyrometer-type thermoregulator.

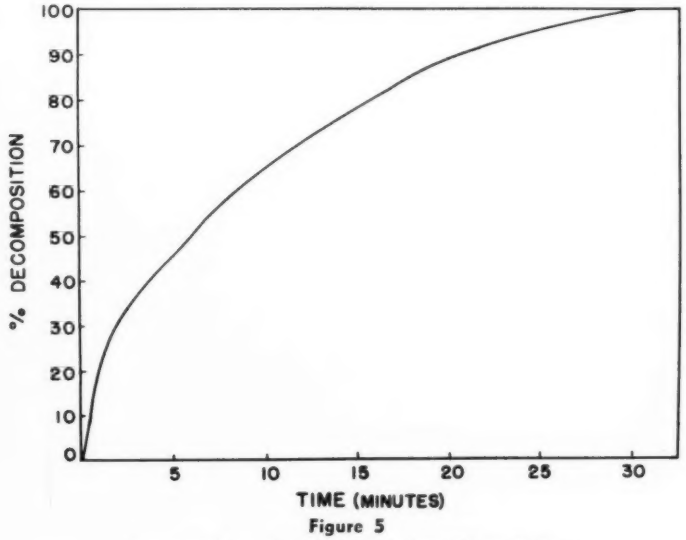

Figure 5

Decomposition of Calcozine Yellow OX at 250°F as calculated from Figure 4

USES

The High-Temperature Dyeometer has been found to be adaptable for the study of any reaction taking place at temperatures up to 300°F in a liquid system where measurable spectrophotometric changes occur during the course of the reaction. Two of the simplest examples of these involve the stability of dyes in solution and the exhaustion rates of dyes onto various textile fibers under different high-temperature conditions.

STABILITY MEASUREMENTS ——One of the problems in high-temperature-dyeing methods is that of selecting dyes with sufficient stability under high temperature dyebath conditions. Butterworth (*6*), Fowler (*7*), Royer and Zimmerman (*5*), and Coutie et al (*10*) have considered this problem for different classes of dyes in considerable detail. The High-Temperature Dyeometer has been found to provide a particularly convenient method for measuring these stabilities at temperatures up to 300°F.

To measure the stability of a dye in solution, the bath is circulated in the High-Temperature Dyeometer at the desired temperature with the transmission cell positioned in front of the sample beam of the recording spectrophotometer. Spectrophotometric curves are plotted at various time intervals for as long as necessary. Appreciable change in curve shape is an indication of decomposition. Figure 4 shows the set of curves obtained when the thermal decomposition of a solution of Calcozine Yellow

OX (*CI* 655) (50 mg/400 mls H_2O), a basic dye, was measured. These curves were plotted at various time intervals while the dye solution was held at a temperature of 250°F. Assuming decomposition is complete in 30 minutes, these same data are plotted as percent decomposition vs time in Figure 5. It can be seen that this dye decomposes rapidly at 250°F. Since several factors can contribute to changes in transmission curves, the usual precautions in interpreting spectrophotometric data must be kept in mind.

EXHAUSTION MEASUREMENTS ——Knowledge of the rates at which dyes exhaust onto fibers under different conditions is of great importance, particularly where mixtures of dyes are used to obtain the desired shades. The High-Temperature Dyeometer makes it possible to obtain this information directly under any desired set of high-temperature conditions. When the dyebath has reached the dyeing temperature, a spectrophotometric transmission curve of the initial bath is plotted. The dyeing is started by allowing the skein or fabric to drop from the upper section of the Dyeometer into the dyebath. At specific time intervals, as the dyeing proceeds, photometric measurements of the bath strength are made without disturbing either bath or sample. The completeness of the spectrophotometric record of the dyeing process obtained at 230°F with Vat Jade Green on Type 42 Orlon acrylic fiber is shown in Figure 6. The dyebath contained 5 grams of Orlon 42, 0.15 g of dye, 1 oz/gal $Na_2S_2O_4$, 2 oz/gal K_2CO_3 and 400 mls distilled H_2O. Curve A represents the initial dyebath curve before the Orlon 42 was dropped into the bath. Curve T represents the dyebath curve after the dyeing has continued for 90 minutes at 230°F. Curve T shows that the bath was approximately 74% exhausted at the end of this time. The data shown in Figure 6 are presented again in Figure 7 plotted as percent exhaustion vs time.

EXAMPLES OF APPLICATION

The following are some examples from specific studies made in which the High-Temperature Dyeometer was used.

RATE OF CHROMATION AT 230°F——When wool is dyed with chrome dyes, the rate at which the chrome-dye complex is formed in the dyebath during the dyeing operation is important. Frequently the

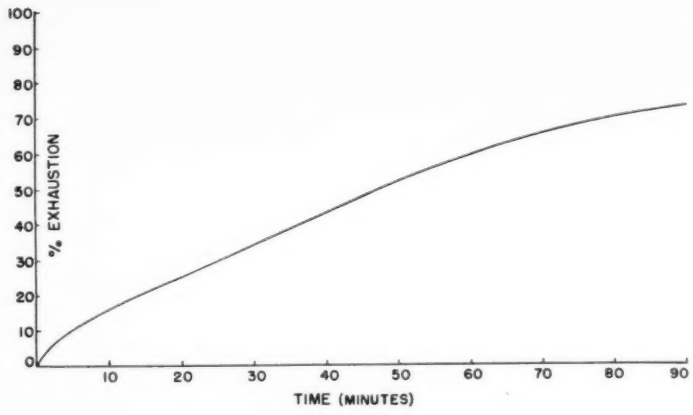

Figure 7

Dyebath exhaustion curve calculated from Figure 6

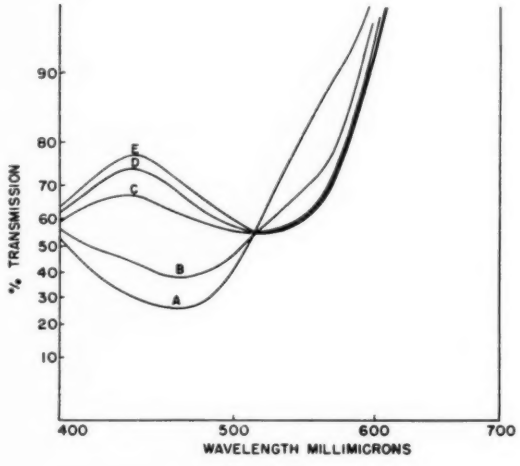

Figure 8

Transmission curves of a solution of Calcochrome Fast Red ECB at different stages of chromation at 230° F

A) Initial transmission curve of unchromed dye
B) Two minutes after the addition of $K_2Cr_2O_7$
C) Five " " " " " "
D) Seven " " " " " "
E) Ten " " " " " "

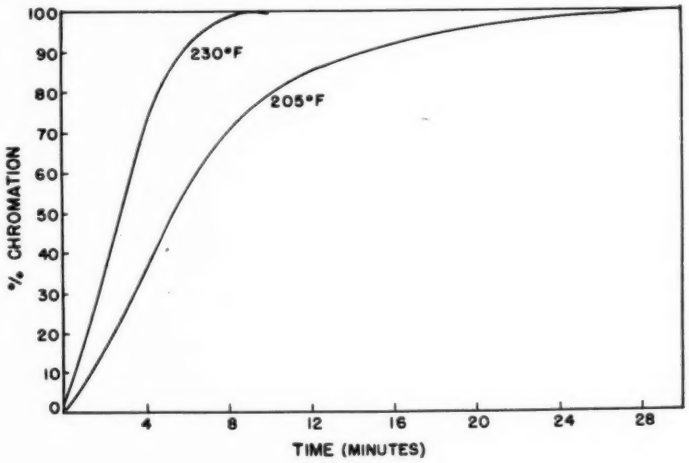

Figure 9

Rate of chromation of Calcochrome Fast Red ECB at a pH of 5.7 following addition of $K_2Cr_2O_7$ to the bath

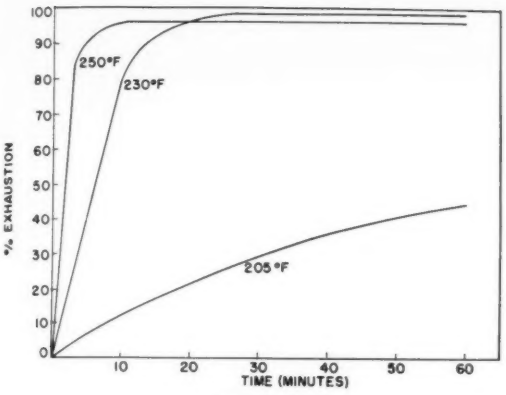

Figure 10

One percent dyeings of Calcozine Magenta XX (*CI* 677) on Orlon 42 at different temperatures

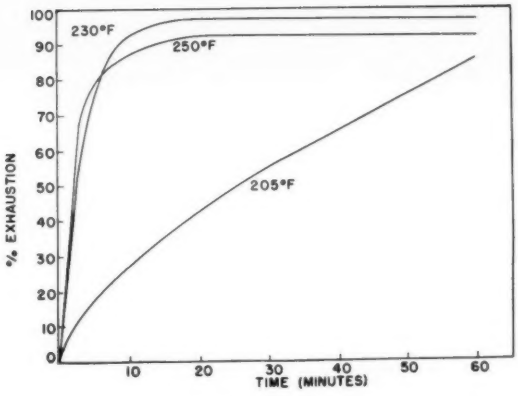

Figure 11

One percent dyeings of Calcozine Blue GXX (*CI* 922) on Orlon 42 at different temperatures

chrome-dye complex is not as readily absorbed by the wool as is the unchromed dye. Therefore, the shade and strength of such a dyeing is affected by the rate of chromation. Since the chrome-dye complexes on the fiber are usually faster to light and washing than the corresponding unchromed dyes, it is important that the dye be applied in such a way that it will be completely chromed in the finished dyeing.

The Dyeometer has proved to be adaptable for making measurements of rates of chromation of dyes (*8*). Such experiments can be carried out by making spectrophotometric records of the dyebath during a dyeing, or during a chromation in the absence of any fiber. The High-Temperature Dyeometer has made it possible to extend the range of these studies to the higher temperatures.

With this new instrument the changes in transmission at high temperatures are easily and exactly observed. This is illustrated by the family of curves in Figure 8 showing the changes which occurred on chroming Calcochrome Fast Red ECB (*CI* 652) at 230°F in the absence of fiber. The dyebath contained 0.050 grams of dye and 0.025 grams of potassium dichromate at a pH of 5.7. Curve A was taken before the addition of $K_2Cr_2O_7$ and represents the color of the unchromed dye. Curve E represents the color of the completely chromed dye formed at the end of 10 minutes. No additional change in the curves occurred after 10 minutes at 230°F. The intermediate curves correspond to the intermediate colors of the bath during the chromation. From these curves the percentage of chromation at various times was calculated. The results are plotted in Figure 9 along with similar chromation rate data obtained at 205°F. It can be seen that the rate of chromation at 230°F is more than twice as fast as the rate of chromation at 205°F.

An examination of the curves in Figure 8 shows that they have a common crossing point (isosbestic point) at approximately 520 millimicrons. When exhaustion rates of this dye must be measured under conditions such that chromation also occurs during the dyeing, transmission measurements at this wavelength will provide reliable exhaustion values although the curve shape becomes quite different.

EXHAUSTION OF BASIC-TYPE DYES ON ORLON 42——A number of basic dyes exhaust on Orlon 42 relatively rapidly at temperatures within the range of open equipment. As a rule, however, the increase in dyeing rate obtained by a rise in dyebath temperature from 200° to 212°F is quite great. This increase in rate continues at temperatures above the boil and temperatures as high as 230°F are often recommended. For that reason it is important to know the exact dyeing behavior in the higher temperature range. Dyeings were made of a number of basic dyes using 0.5% glacial acetic acid (owf) and 0.3% sodium acetate (owf) in the bath. Calcozine Magenta XX (*CI* 677), the exhaustion curves for which are shown in Figure 10, is typical of colors which exhaust slowly at 205°F. However, some dyes, like Calcozine Blue GXX (*CI* 922), exhaust very well at 205°F. The exhaustion rates of this dye are plotted in Figure 11. It can be seen from Figures 10 and 11 that, while the initial rate of exhaustion at 250°F was greater than the initial rate of exhaustion at 230°F, the final exhaustion at 230°F is slightly greater than the final exhaustion at 250°F. This probably can be explained by the fact that the dyeing processes are exothermic, and for a given set of conditions the amount of dye on the fiber at equilibrium must decrease with increasing temperature.

As a general rule a dyeing carried out at a lower temperature will require a much longer time to reach

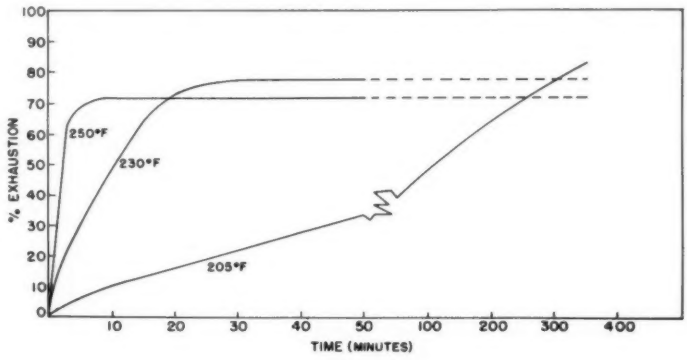

Figure 12

Exhaustion curves of 2% dyeings of Calcozine Green (*CI* 657) on Orlon 42

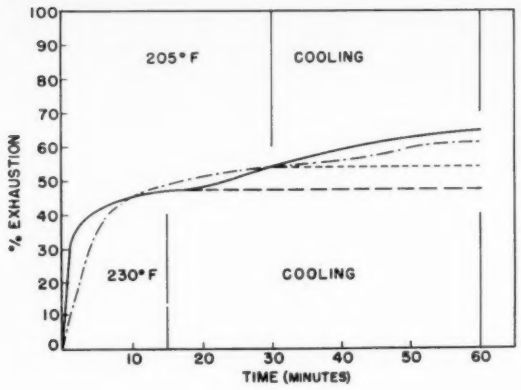

Figure 13
Exhaustion curves of 2% (owf) dyeings of Calcodur Orange EGL (Pr 72) on cotton
Dyeing started at 205°F ——————
Dyeing started at 230°F ——————

equilibrium, but the final exhaust will be greater at the lower temperature. For that reason the selection of dyeing temperature needs to be made with both dyeing rate and equilibrium exhaust in mind. This relationship is illustrated by the curves in Figure 12, which show the exhaustion curves of a 2% dyeing of Calcozine Green V (*CI* 657) on Orlon 42. It can be seen from the curves that the dyeing at 250°F came to equilibrium in about 10 minutes with an equilibrium exhaust of 71%. The dyeing at 230°F came to equilibrium after 30 minutes with an exhaust of 77%. After 345 minutes the dyeing at 205°F had exhausted 81% of the dye and still had not reached equilibrium.

STUDY OF DIRECT DYES ON COTTON AT HIGH TEMPERATURE ——The dyeing of cellulose at high temperatures has been discussed in a number of recently published papers. Butterworth (*6*) divided the direct dyes into three groups based on their stability. An additional summary of direct dyes on cellulosic fibers was presented by Fowler (*7*), and recently Schmidt (*9*) showed that the stability was related to the chemical nature of the dyes.

In general the high temperature does not have as marked an effect on exhaustion on cotton as is observed with some classes of dyes on the hydrophobic fibers. Nevertheless there are worthwhile advantages to be obtained by the use of higher dyeing temperatures. Outstanding among these are better penetration and better levelness, particularly in package dyeing. As has been stated previously, the equilibrium exhaust is generally less at higher temperatures. For that reason the common practice of completing the dyeing in a cooling bath to increase the exhaustion is to be recommended. Data on exhaustion rates of direct dyes at the higher temperatures are needed whenever such dyeing methods are being considered. The High-Temperature Dyeometer is readily used to measure the exhaustion rates of direct dyes. Dyebath observations do not provide any information regarding the leveling obtained at high temperatures. However, a study of exhaustion is illustrated in Figure 13, which shows the exhaustion rate curves of two dyeings of Calcodur Orange EGL (Pr 72) on cotton. Each dyebath contained 2% dye (owf) and 20% NaCl (owf). The liquor ratio was 40:1. One curve represents a dyeing started at 205°F while the other represents a dyeing started at 230°F. Both dyeings were finished in cooling baths. From the curves it can be seen that, while the initial rates are fast, there is a measurable difference, the rate being greater at 230°F. Since the dyes level better and penetrate faster at the higher temperature, the cooling bath step may be started sooner when the dyeing is started at the higher temperature. There was no appreciable difference in exhaustion in these two cases after 10 minutes of dyeing, however. The horizontal dashes show the projected exhaustions, which would have been obtained in constant-temperature baths. The broken and solid curves show the actual data from cooling baths, the cooling bath stage beginning after 15 minutes for the 230°F dyeing and after 30 minutes for the 205°F dyeing. It can be seen from the curves of Figure 13 that the bath reached equilibrium in about

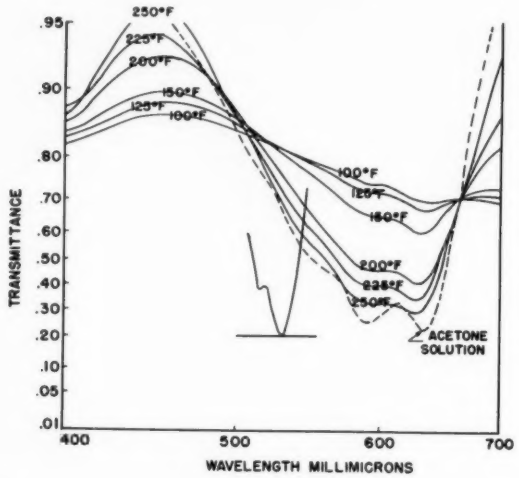

Figure 14
Transmission curves of a dispersion of Calcosyn Sapphire Blue 2GS Conc (0.1 g/400 ml H_2O)
The curves were plotted as the temperature was raised from 100° to 250°F.

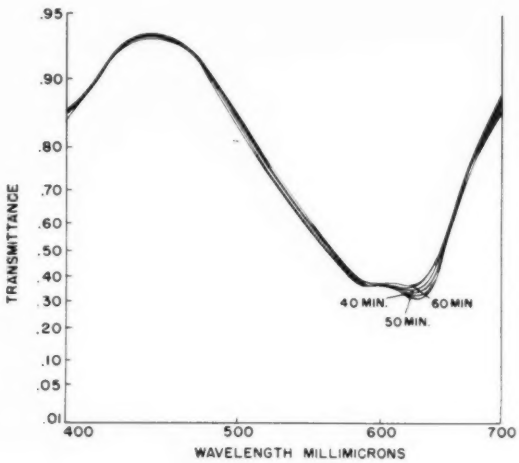

Figure 15
Calcosyn Sapphire Blue 2GS Conc—Heated at 230°F for one hour

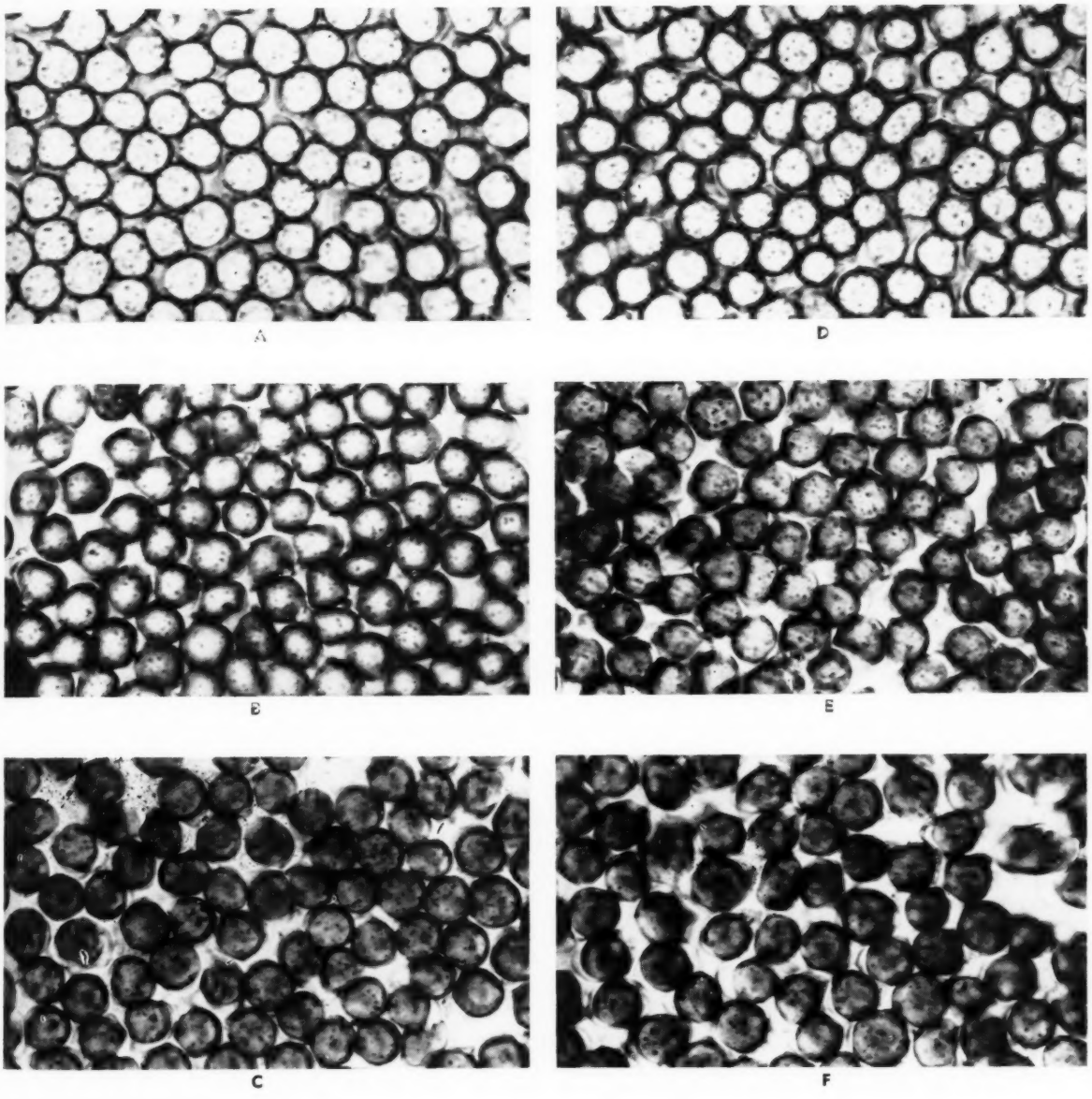

Figure 16
Cross sections of 5% owf dyeings made for one hour at 200°, 230° and 250°F

A—Calcosyn Sapphire Blue 2GS Conc at 200°F		D—Calcosyn Violet B at 200°F	
B— " " " " " " 230°F		E— " " " " 230°F	
C— " " " " " " 250°F		F— " " " " 250°F	

15 minutes at 230°F, whereas 30 minutes were required at 205°F.

STUDIES OF DISPERSE DYES AT HIGH TEMPERATURE—STABILITY MEASUREMENTS———The stability of disperse dyes can be measured in a manner similar to that used for soluble colors. Appreciable changes in the curve shape of a dispersion is an indication of decomposition. Care must be taken, however, when using transmission measurements with dispersions since such data are reliable only as long as there is no change in the character of the dispersion. The shapes of the transmission curves of many dispersions change, when held at a high temperature. Generally this is not due to any decomposition but rather to an improvement in the degree of dispersion which may even approach that of a solution. Figure 14 shows the transmission curves of a dispersion of Calcosyn Sapphire Blue 2GS Conc (Pr 228) at different temperatures from 100° to 250°F and also shows the curve of an acetone solution of this dye.

It can be seen that the transmission of the dispersion became more like that of the solution as the temperature increased. This shows that the dye became progressively less aggregated although, even at 250°F, the dye did

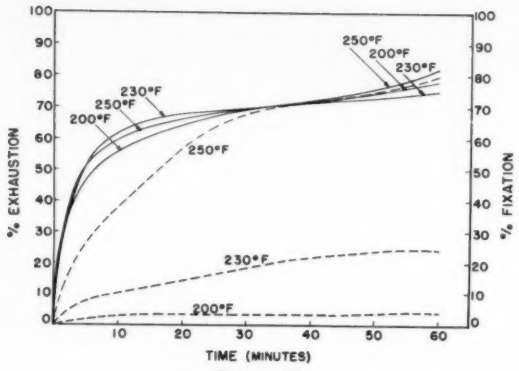

Figure 17

The curves point out the difference between the dye exhausted and dye fixed when dyeing Calcosyn Yellow 7G Conc on Dacron. The broken curves represent the dye fixed (not removed by soaping). The solid curves represent the dye exhausted.

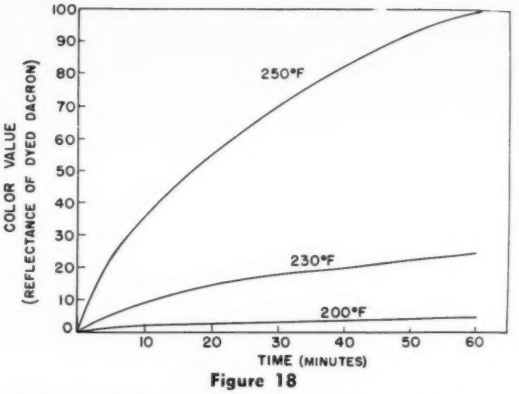

Figure 18

The dyeing made at 250°F for 60 minutes was the standard (100%)

not form a true solution. Figure 15 shows the transmission curves of a similar dispersion of the same dye taken every five minutes while the bath was held at a temperature of 230°F. There is only a small change in the shape of the curve during 60 minutes at 230°F. From this it is apparent that the degree of dispersion at constant temperature was fairly constant. Even in this case, however, exhaustion rate measurements made from the dispersed dyebath would be open to question because the quality of the dispersion could be changed by the dyeing process. For these reasons it is considered more reliable to use other provisions when working with disperse dyes.

A better method for measuring the stability of disperse dyes at high temperatures is to draw off samples of the dispersions at different time intervals, and dissolve each in a suitable solvent, before measuring it spectrophotometrically. The High-Temperature Dyeometer is equipped with a special valve for drawing off samples of the dyebath in situations such as this.

EXHAUSTION MEASUREMENTS ——Since, as discussed above, the transmissions of dye dispersions may not provide reliable quantitative data, the transmission cell of the High-Temperature Dyeometer can be replaced with a valve which permits small portions of the circulating bath to be drawn off. Accurately measured samples are dissolved in carefully measured volumes of a suitable solvent, and the concentrations of the resulting dye solutions measured spectrophotometrically. The final values are plotted exactly as is done in the case of soluble dyes.

THE EXHAUSTION OF DISPERSE DYES ON DACRON POLYESTER FIBER——The disperse dyes have been used, in conjunction with a dyeing assistant, for dyeing Dacron at temperatures below 212°F. When higher dyeing temperatures (above 212°F) are used, the dyeing assistant (carrier) is usually omitted entirely or used in much smaller amounts.

In studying the application of disperse dyes to Dacron, it was found that the higher the dyeing temperature (200° to 250°F) the greater the amount of dye which became fixed on the fiber during a normal dyeing period. This holds true only when the dyes are stable at the higher temperature. Figure 16 shows cross sections of Dacron fibers dyed for one hour at 200°, 230°, and 250°F with Calcosyn Sapphire Blue 2GS Conc and Calcosyn Violet B Conc. These dyeings were made with 5% of dye (owf). These cross sections show the increased fiber penetration which resulted from the use of the higher dyeing temperatures.

It is important to keep in mind that, in the dyeing of Dacron with disperse dyes, exhaustion data often are not a satisfactory indication of how much dye is fixed on the fiber. In many cases a large proportion of the dye which exhausted from the bath during dyeings carried out at 200°F, or even at 230°F, is attached to the surface of the fibers only and later washes off. Usually the dye which exhausts onto the Dacron at 250°F is well penetrated and fixed, and remains in the fiber through the severest washing. Figure 17 shows the exhaustion curves (solid lines) and also the fixation curves (broken lines) of a 5% (owf) dyeing of Calcosyn Yellow 7G Conc at 200°, 230°, and 250°F. It can be seen from these curves that the dye exhausted from the bath onto the Dacron at a similar rate at all three temperatures. However, the fixation curves show that at 200° and 230°F, only a small amount of the exhausted dyes was actually fixed. To determine the amount of dye fixed at the end of any time interval, the Dacron was thoroughly soaped to remove all surface dye. The fixed dye was then extracted from the Dacron by refluxing the dyed sample in pyridine and the resulting pyridine solution measured spectrophotometrically.

It can also be seen from Figure 17 that there was more dye fixed on the Dacron in 5 minutes at 230°F than was fixed in 60 minutes at 200°F and, there was practically the same amount of dye fixed in 5 minutes at 250°F as was fixed in 60 minutes at 230°F.

The color values of the dye samples were roughly proportional to the amounts of dye fixed and showed no relationship to the dyebath exhaustion. This is shown in Figure 18 in which the color values of dyed skeins are plotted against dyeing times at different temperatures. Using the 60-minute dyeing at 250°F as the standard (100%) the color values of the other dyeings were calculated from their reflectance values read with a spectrophotometer.

Additional detailed studies of the dyeing processes, at high temperatures, of different classes of dyes on different fibers are in progress.

LITERATURE CITED

(1) Waters, *J Soc Dyers Col* **66**, 609 (1950).
(2) Robinson, R D, and Zimmerman, C L, *Am Dyestuff Reptr* **39**, 250 (1950).
(3) Philadelphia Section, AATCC, *ibid* **38**, 9 (1949).
(4) US Pat 2,405,167.
(5) Royer, G L, Zimmerman, C L, Walter, H J, and Robinson, R D, *Textile Research J* **18**, 598 (1948).
(6) Butterworth, K, *J Soc Dyers Col* **69**, 362 (1953).
(7) Fowler, J A, *ibid* **71**, 443 (1955).
(8) Kienle, R H, Royer, G L, and McCleary, H R, *Textile Research J* **16**, 616 (1946).
(9) Schmitz, A, J Soc Dyers Col **71**, 910 (1955).
(10) Coutie, G A, Lemin, D R, and Sagar, H. *ibid* **71**, 433 (1955).

Proceedings of the
American Association of Textile Chemists and Colorists

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JUNE 4, 1956

Future Papers

Manuscripts of the following papers, all of which have been presented before local sections of AATCC, have been submitted to date to the publishers of American Dyestuff Reporter. Subject to the approval of the AATCC Publications Committee, all will appear in the Proceedings in future issues.

Authors and Section Officials are requested to inspect this list, and notify the publishers if there are any omissions.

"Colorimetric Evaluation of Color Gradients in the Woolen & Worsted Industries"—Roland E Derby, Jr, The Derby Co, Inc

"The Application of Vat Dyes to Acrilan and to Acrilan Rayon Blends"—Edgar D Smith and Walter H Hindle, The Chemstrand Corp

"Practical Interpretations of the Results of Laboratory Investigations in the Field of Vat Printing"—Maurice R Fox, Arnold, Hoffman & Co, Inc and Imperial Chemical Industries Ltd

"Chemical Considerations of Woolen and Worsted Finishing"—Herbert C Haller, S Stroock & Co, Inc

"Some Aspects of the Newly Developed Crypto-Anionic Surface-Active Agent"—H G Seifert, Sandoz Chemical Works, Inc

"Hibulk Acrilan"—S Jack Davis, The Chemstrand Corp

"Arnel Triacetate—Its Properties, Applications and Dyeing Characteristics"—A F Tesi, Celanese Corp of America

"The Dyeing and Related Processing of Nylenka"—Ross M Stribling, American Enka Corp

"Cotton Textiles: An Over-Capacity Industry?"—W E Clark, U S Rubber Co

"Cotton Finishing"—Hector C Borghetty, Rohm & Haas Co

"Arnel—1956"—Fred Fortess, Celanese Corp of America

"A Study of Wash and Wear Cottons"—Charles R Williams, Monsanto Chemical Co

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THE Publications Committee of AATCC has adopted the following resolution:

"The Association strives to maintain a high scientific and professional standard for papers delivered at meetings and subsequently published. Speakers and authors must make every effort to avoid the use of trade names, commercial products or process names wherever such use may be construed as advertising. Wherever possible, scientific nomenclature must be employed. It is recognized that in some instances trade names are necessary to avoid lengthy description. Certain trade names have been so widely used as to become generic and these normally are permissible. Further, some technical papers may involve the presentation of a new product or process wherein trade name reference is obligatory.

"Giving due consideration to such valid exceptions, it is incumbent upon the author to maintain the proper scientific attitude, avoiding any expressions or devices aimed at promoting a particular product or process.

"Questionable papers are to be referred to the chairman of the Publications Committee, who will submit them to an editorial board which would be appointed as needed. The Board would report to the Publications Committee, which would have the final voice in accepting or rejecting a paper."

"Aesthetic Standards in Textile Print Designs"—D D and Leslie Tillett, House of T Fabrics

"Wash and Wear Finishes on Cotton Fabrics"—Hector C Borghetty, Rohm & Haas Co

"Wash and Wear Fabrics"—E W Lawrence and R H Phillips, Cranston Print Works Co

"New Paper Products in Competition with Textiles"—Robert B Hobbs, National Bureau of Standards

"Current Developments in the Application of Dyestuffs"—L S Thompson, General Dyestuff Co

Employment Register

This column is open for two insertions per year, per member, without charge. Blanks can be obtained from, and filed with, the secretary of the Association, Post Office Box 28, Lowell, Mass. It is understood that these will be open to inspection by prospective employers who can obtain further information from the secretary.

56-5

Education: Dyeing and finishing graduate.

Experience: Chemist, supervision, technical service. Work simplification, correspondence, etc.

Age: 38; married; references; desires position in sales, production or laboratory. Prefers Mid Atlantic or New England. 5-21, 6-4

56-6

Education: B S, Chemistry and dyeing.

Experience: Textile chemist

Age: 23; single; references; position as textile chemist desired, research or technical service, vicinity of New York City. 5-21, 6-4

56-7

Education: Graduate of college night course in chemistry.

Experience: Superintendent of dyeing and finishing specializing in tricot.

Age: 47; married; references; position in supervision of dyeing or finishing desired, South or West. 5-21, 6-4

56-8

Education: College graduate, Spain, industrial chemistry; year at Massachusetts Institute of Technology in chemical engineering.

Experience: textile chemist, USA and presently Spain; publications in Spanish

Age: 32; single; references in USA; position desired in New England or in Central or South America, chemist or sales. 5-21, 6-4

Rhode Island Section ——

TEXTILE CHEMICAL SPECIALTIES—THE MAGIC SKIN*

MARK WEISBERG
Eltex Chemical Corp
Providence, R I

The author presents a picture of today's textile chemical specialties business, citing personal experiences, statistics, and problems, frequently in a light vein.

He concludes with a brief look at trends in the business.

INTRODUCTION

THIS OD shade you see on my face is a Florida product. I got back only yesterday. I don't mind telling you it is the most expensive coloring matter per square inch you'll ever be called upon to produce. What is more, as you can see, it is very uneven. There are no wetting or leveling agents in Florida; specialty salesmen do not travel that far South. The shade is known as ODFS 28-35. FS, as you might guess, stands for Florida Sunshine. The 28-35 stands for the range of temperature in Florida in January, while the North had a range of 45-55.

Tonight, for about 5 minutes, let's imagine that I am an important purchasing agent for a very large textile mill and you are specialty salesmen. You call on me and I indifferently invite you to my office. You start by telling me of a wonderful wetting and leveling agent you are offering. I say, "Oh, no! Not another one. I already have the best. I use the SSW brand." You say, "What is that?" And I say "Why, don't you know that SSW stands for Split Second Wetting?" Are you stumped? Not at all. You say, "We have the VP wetting agent, a much better one. VP stands for Vapor Phase. All you have to do with my product is put a few ounces in a bottle, hang the bottle by a string in the dye room and all your dyeings will come out perfectly level until the wetting agent evaporates." So I say, "That sounds fine. Send me a 5-gallon sample free of charge and come around next year for an order." This, ladies and gentlemen, may be a gross exaggeration, but seriously, haven't wetting and leveling agents improved in quality and become much lower in price than, say, 15 years ago? Think of the Deceresols, Tritons, amine condensates, and fatty alcohol sulfates.

Next you timidly offer me some urea-formaldehyde resin. There I fool you. I offer you a standing order for a carload a week. You are duly surprised and wonder whether your boss will fire you for taking the order and you ask, "Are you going into a new line? You never used resin in such quantity before." And I tell you, "Yes, we are going into a new line. We are going into the salvage business. We are going to recover the urea and sell it for fertilizer, and the formaldehyde we'll sell to the embalmers. Figure it out. There ought to be as much profit in this as in wet-processing of textiles." Ridiculous? Not at all.

At a time of inflation, when the dollar we knew in 1938 is now worth 50¢ and raw materials costs are the same or even higher, I am buying detergents and wetting agents at half the 1938 selling prices; urea-formaldehyde resin at one-third the price; and water repellents at half. To make a profit, your firm strives for the elusive volume theory, which somehow never is attained. And what do you suppose will happen to profits if the volume drops 10% or 15% as it did lately during the textile slump? I heard many complaints from textile chemical specialty manufacturers at that time.

Why this terrific competition? I don't know. It may be due to many factors—larger volume consumption, more efficient production methods; and, perhaps, too many specialty manufacturers. It is a significant fact that in many industries associations are formed to find solutions for their common economic problems, but the textile chemical specialty manufacturers never succeeded in getting together for the betterment of their industry. This may be due to the fact that they are satisfied with things or that they are very rugged individualists.

The textile industry is the largest consumer of chemicals; it consumes roughly 25% of the chemicals produced in the United States, or a little over one billion dollars' worth. No other industry comes anywhere near this figure. The steel industry consumes about 9% of the chemical production; the rubber industry about 7%; food and drugs about 7%; together these three industries use less than the textile industry does. In fact, the textile industry is chiefly responsible for the growth of the chemical industry. And, this is undoubtedly the reason for the chemical industry following the textile industry South. I believe if Horace Greeley were around today he would say, "Go South, my son, go South." This would hold particularly true for the textile chemical specialty manufacturer. Most of the textile chemical specialties are made in the North, but there are a number of growing firms in the South which will become strong competition before long.

EXTENT OF THE TEXTILE CHEMICAL SPECIALTIES BUSINESS

How big is the textile specialty market or, rather, how large a portion of this one billion dollars' worth of business is represented by textile chemical specialties? Well, first we should define a textile chemical specialty. Certainly the sodium alkyl aryl sulphonated detergents are no longer specialties, nor are the lauryl alcohol sulfates. Even urea-formaldehyde resin, the unmodified one, is no longer a specialty. The best definition I can arrive at is that a textile chemical specialty is a compound or product developed to do a special job for a special type of fiber or fabric. It is that chemical product put on textiles to provide the "magic skin" that upgrades the textile and makes it sell.

There are no statistics on the value of textile chemical specialties sold, but one can arrive at an approximation by difference—by finding out how much organic and inorganic chemicals, which are not specialties, the textile industry uses. The man-made fibers alone, which are wholly chemical, represent a consumption of half that billion dollars' worth of chemicals used by the textile industry. The dyestuff industry, which produces 200 million dollars worth of

*Presented before the Rhode Island Section on January 26, 1956.

dyes, sells 85%, or 170 million dollars' worth, to the textile industry. In 1953 the textile industry used the following:

60%	of 2 billion pounds of synthetic detergents
1.75	billion pounds of starches
45	million pounds of 30% peroxide
2	billion pounds of caustic soda
170	million pounds of sulfuric acid, exclusive of rayon use
130	million pounds of soda ash
60	million pounds of chlorine
$50	million of soap, glycerine and related products

Rayon production alone in 1953 called for:

1	billion pounds of caustic soda
1	billion pounds of sulfuric acid
1	billion pounds of cotton linters and wood pulp
300,000	pounds of carbon disulfide

And acetate production in that same year called for:

500	million pounds of acetic anhydride
90	million pounds of acetone
1	billion pounds of acetic acid (some recovered)
16	million pounds of sulfuric acid
200	million pounds of pulp

Therefore, my estimate is that the textile chemical specialty business amounts to $70 to $80 million annually. This amount must be distributed among about 100 specialty manufacturers who cater to the textile industry.

The number of products made is bewildering. The textile chemical specialty business is like no other specialty business unless it is the manufacture of textiles themselves. There is no uniformity in textile goods nor in the treatment they receive; hence, there is no wide market for any one specialty. The *AATCC Year Book* lists 3400 tradenames of 70 different types of chemical specialties. These same statistics were mentioned in an article by Robert W Philip, of Callaway Mills, La Grange, Georgia (*1*). But, Mr Philip is not a textile specialty manufacturer. We in the field know that these 3400 tradenames represent less than 10% of the specialties actually on the market. In my former company we made about 300 specialties but listed only 12 in the *Year Book*. A recent article (*2*) on the interrelationship of the textile and chemical industries carried a picture of a specialty plant which boasted that it makes 500 distinct items; yet the *Year Book* lists only 67. And this company believes in free as well as paid publicity.

The 3400 specialties listed in the *Year Book* are classified by Mr Philip (*1*) as follows:

Finishing agents and assistants	448
Dyeing assistants	430
Detergents and assistants	397
Wetting agents	280
Softeners	242
Lubricants for textiles	212
Emulsifying agents and assistants	202
Dispersing agents	198
Sizing agents	153
Kier-boiling agents	150
Printing assistants	111
Bleaching assistants	110
Resins	102
Fulling agents	82
Water repellents	76

And, as I said, these should be multiplied by a factor of a least 10 to get the true picture.

True, many of these are duplicates, but they do differ from one manufacturer to another. Everyone wants a different "magic skin." One mill wants a soft water repellent; another a stiff finish; acetates call for a water repellent that will not mark off; resin treated goods require a water repellent that will penetrate the hydrophobic film. Recently a large manufacturer of textiles developed a new fabric and required a finish that would be permanently water repellent, mildewproof and fireproof, to be applied from one bath. Any takers?

PROBLEMS OF THE TEXTILE CHEMICAL SPECIALTIES MANUFACTURER

The headaches the specialties manufacturer encounters and the variety of products he must produce are, of course, due to the constant change taking place in the textile industry. The industry is becoming more complex, and the specialty business must meet the demands made on it. It is no longer a matter of cotton, wool, and silk fibers, but about 22 additional man-made fibers and hundreds of blends of these with themselves and natural fibers. Add to this the variety of fabrics, the variety of construction, styles, end use, etc, and you get an idea of the interesting and "charmed" life the textile chemical specialty manufacturer lives.

An additional difficulty is that special finishes or assistants must be developed on short notice. There is no time for long range research. It may take years for the textile technologist to develop a new fabric. It may take months to produce samples in the weave shop. But, the dyer and the finisher must produce results in a matter of weeks or days. The finisher, in turn, puts the pressure on his favorite supplier. The supplier may spend thousands of dollars to develop a desired result, but he has no guarantee that the new textile will sell or that a competitor will not match his finish and take his business away from him. For example, some years ago a mill developed a continuous method of scouring, deoiling, bleaching, souring, etc. The mill required a solvent emulsion that would not break on the alkali or acid side and do a good deoiling and degreasing job. We perfected one and held the business for three months. Then a competitor produced a better product and we lost the business, which was substantial. Within two months we got the business back by further improving our product. The business kept going from one supplier to the other every three months for the next two years. By then the mill learned enough from its two suppliers to duplicate the product, and both suppliers were out.

I stated earlier that textile specialties differ from most other specialties chiefly because there is no broad general demand for any one specialty, as there is in other fields. For example, in the cosmetic industry a man developed a cream shampoo; he had over 50 million potential customers. His product was not an original one—it used the same lauryl sulfate that is used in liquid shampoos—yet in three years from a modest start he sold out for nearly $5 million. A manufacturer of a home-permanent-wave kit, beginning in the same way, sold out for $19 million in less than four years. I need not tell you about such specialties as scotch tape or bubble gum. We have one important process for the metal industry—a blackening process for steel called Jetal—which we have been marketing for 20 years. This specialty will blacken steel in any form from a phonograph needle to an airplane propeller. In other words, it has wide universal application to anything made out of steel. No such universal specialty exists for all cotton.

It is highly significant that hardly any textile specialty manufacturer ever built up a business of much over $3 million per year. Most of them are in the less-than-$1-million class. A few did grow, but did so only by diversification into other fields, such as dyes, cosmetics, sanitation, agriculture, paper, leather, or into a general field of chemicals for the chemical industry itself with such products as chelating agents, etc.

PERSONAL EXPERIENCES

Now I'd like to become a little autobiographical. I make no apology for this for several reasons. First, people like to listen to personal experiences; second, these experiences involve 37 years in the manufacture of chemicals, chiefly for the textile industry, from dyestuffs to specialties; and, third, this period parallels the period of the greatest development of the chemical industry in the United States and of textile chemical specialties in particular.

My first 11 years out of college were spent in the manufacture of dyestuffs. In 1933, after selling my

dyestuff business, I started a textile chemical specialty business. As many of the old timers know, specialties in those days consisted mainly of sulfonated tallow, cream softeners, sulfonated olive oil foots, castor oil, oleic acid, and many variations of these with pine oil, cresylic acid and pyridin. The term "surface-active agents" was hardly known, much less cation softeners, nonionics, resins, plastisols and hundreds of other modern specialties. In making my decision to enter this field I resolved to confine myself strictly to synthetic specialties and keep away from the sulfonated natural products made by many, too many, manufacturers. This was not an easy task for a small outfit with a staff of two chemists.

We started with the low molecular alkyl naphthalene sodium sulfonates; the isopropyl butyl and amyl naphthalenes. These were first described in the German literature around 1912 and marketed in this country in the late 1920's under the name Nekal BX. These were the first synthetic surface-active agents to be introduced to the textile industry. Strange as it may seem, these original products are still manufactured in large tonnage quantities in spite of the tremendous number of new "super" surface-active agents now on the market. Their chief virtues are stability and versatility. They are good wetting agents; they are stable at all temperatures and all pH's, except strong caustic, which only salts them out; they have good dispersing and hydrotropic properties; they are stable in strong sulfuric and, therefore, widely used in carbonizing. Just recently, other industrial uses have been found for them, which may even further increase their production.

One of our more successful products was an amine condensate of coconut oil—and a very unique product it was, indeed. It was the only synthetic detergent of American origin, patented by the late Wolf Kritchevsky. I knew Dr Kritchevsky well, and became interested in his patent. In our laboratory we ran through 20-odd examples cited in the patent and picked one product for testing. By sheer luck we picked the right one for textile use. We gave this oily condensate to the only textile chemist we had then and asked him to tell us what it was good for. His report, in 1937, was to the effect that he could not find a problem in textile operations that the product was not good for. He reported that it was a good wetting and rewetting agent, a good detergent in the presence of soda ash, an excellent lime dispersant, a good leveling agent for vats, a good stripping assistant, a good kier boiling compound, that if left in the goods it would not go rancid and would not interfere with subsequent treatments, and that it had some softening properties. In fact, it was the answer to a textile mill's prayer; one product good for all ills that befall a wet processor. We were the first to introduce the product and sold more than a half million pounds the year before the war. During the war, due to the shortage of amines, sales dropped; and, after the war, every textile chemical specialty manufacturer got into the act. Today there are many variations of the original product and millions of pounds are produced. One variation, used by the large soap makers as a foam stabilizer, has reached a volume of over 50 million pounds a year. Lately it has been used either for acid or alkali fulling of wool. When it is used as the lubricant for fulling the carbonized wool, it also serves as the scouring agent after fulling and no additional soap or detergent is needed. Hundreds of other specialties based on this amine condensate are on the market.

Other successful products of ours were the chelating agents, on which we started work in 1948. Here was an excellent specialty, which had universal appeal. Today there is hardly an industry not using a chelating agent—from textiles to my lady's shampoo, from the mining industry to the embalmer. You have probably noticed how much better corpses look these days. In the textile industry it has helped to solve many difficult problems; it has helped in the softening of water, in the elimination of iron which caused dulling of shades; it has brightened up dyeings considerably. We made these products under license but much original work went into the development and testing of many new products for specific uses. It is interesting to note that the patent we worked under lay dormant for 12 years and very little attention was given to the unique properties and uses of these products until we came into the field. Before 1948 less than $100,000 worth was sold; in 1955 sales were about $6 million, and the use is still growing.

The cationic softeners were brought out by us in 1937. These were looked upon with a great deal of suspicion. They often yellowed whites, changed shades of dyeings, lowered light fastness, and their solubility was poor. Today there are many manufacturers of these cationics, and most of the objectionable features have been overcome. The latest development is cold-water solubility, complete non-yellowing, and practically no chlorine retention. The newer products are also superior, not only on rayon but on cotton and synthetics.

Around 1940 we decided to do some original research. Here we succeeded, but got burned at the same time. We dreamed of riches but got our skin shrunk not once but several times. Improper research can lead to failure as soon as any other form of mismanagement.

You probably guessed that the subtitle of my talk—The Magic Skin—referred to finishes or, as the chairman suggested, that it might have something to do with Marilyn Monroe. But, actually I had in mind Balzac's novel called "The Magic Skin." This story tells of a young talented Frenchman's desire to get rich, famous, and popular fast. He had no patience to work for this. He was so discouraged by his inability to get rich quick that he decided to commit suicide. On the way to the Seine River he passed an antique shop and decided to loiter a while. The shop was presided over by an old wise man who recognized that the young man was in trouble. He invited the young man to a back room and soon had his story—that he was on the way to jump into the Seine and end it all. The old man then showed him a skin which he called "a magic skin" and said that whoever possessed this skin had only to rub it, make a wish, and it would be granted. The young man felt he had nothing to lose, so he bought the skin. However, there was a catch. With every wish the skin would shrink and when it shrank to nothing the possessor of it would die.

It has often occurred to me that every textile chemical specialty manufacturer is the possessor of such a magic skin. The great discoveries he makes in the laboratory give him hopes of grandeur, fame and riches only to discover, when he gets to the wise, hardened textile mill operators, that something went wrong; there are no riches and his skin is shrunk.

Our research led us into dreams of a rosy future many times, only to have our skin shrunk in despair and to see our business nearly die. As early as 1937 we found that, by padding cotton print cloth with 7%—not 6% or 8% but 7%—glycerine, we got a 10% to 50% increase in color value depending on the dyestuff. This meant a big saving in the cost of the dyestuff. We proved our claims by running thousands of yards. While waiting for the mill's decision, we dreamed of

(*Concluded on page P380*)

Midwest Section ——

USE OF SILICONES IN THE TEXTILE INDUSTRY*

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R A Ford

A discussion is given of some of the chemical and physical properties of the silicones when used as textile finishes. The properties and commercial development of the silicones for use as finishes for upholstery and wool fabrics are especially emphasized.

A silicone process for producing shrink-resistant wool fabrics is also described. Advantages claimed are ease of application and unimpaired physical properties of the treated fabrics.

INTRODUCTION

OF all the plastics that the first half of the Twentieth Century has brought forth, silicones are certainly one of the most exciting. They appeal to the chemist as an entirely new class of high polymers based on silicon and oxygen atoms instead of on carbon-to-carbon linkages of the more familiar organic plastics. They fire the imagination of engineers because they go a long way towards filling the gap in durability between the organic plastics and the inorganic crystalline compounds. And they appeal to the ultimate consumer because their unusual combination of properties enhances the performance of many of the things he buys.

The original research into the field of silicone chemistry was instigated by Professor F S Kipping in Nottingham, England, in 1907, who discovered that long-chain polymers could be made containing silicon and oxygen atoms and alkyl radicals. On February 17, 1943, the Corning Glass Works and The Dow Chemical Company jointly announced the operation of the first production facilities for commercial manufacture of silicone products. Since that time, a great amount of progress has been made in utilizing the exceptional properties of these materials by many people in the textile industry.

GENERAL NATURE

WHAT ARE SILICONES? —— Silicones are distant chemical relatives to glass in the sense that silica or sand is their common ancestor. There the resemblance ends, even though glass is the oldest, and still by all odds the most important, plastic engineering material, and though there are moldable plastics in the silicone family. Silicones exist as fluids, lubricating greases, insulating compounds grease-like in consistency but nonmelting, foam-killing compounds, resins for protective coatings, electrical insulation and varnishes for transformers, generators and motors that can run hot or wet without failure, rubber-like silicones that stay flexible at —120°F and don't melt or harden at 500°F, and water repellents for treating fibrous glass, masonry, paper, leather and textiles.

CHEMISTRY——It is easier to picture what silicones do than to tell in nonchemical language what they are. The chemist will tell you that silicones are organo-silicon oxide polymers, or organopoly-siloxanes. In his shorthand molecular algebra, silicones have the formula

$$\left[R_n \, Si \, O \left(\frac{4-n}{2} \right) \right]_x,$$

where "n" can be any number from more than zero to not more than 3 and the entire group, or "x," can be repeated from 2 to infinity. Freely translated, this means that every silicon atom is linked to every other silicon atom through an oxygen atom, and all linkages not satisfied in this way are taken up by organic groups linked to silicon. Chemists recognize this as a very durable molecular arrangement, which resists the ravages of heat, time, and weather. The properties of the silicones in their physical forms bear this out.

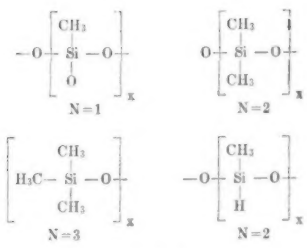

Figure 1

Figure 1 illustrates the possible molecular "building blocks," in which "n" varies from 1 to 3 and the methyl group is the organic substituent. Notice that a hydrogen atom may also be substituted. The "building blocks" shown here which have a substitution, or "n" value, of two form compounds called methyl hydrogen polysiloxanes and dimethylsiloxanes. These two compounds and their various combinations are those that have found commercial use as finishes in the textile industry.

SILICONES IN TEXTILE FINISHING

Silicone finishes are clear, solvent-soluble oils and are usually applied in emulsion form to the fabric. As they have a strong tendency to wet all fiber surfaces rapidly, only a very small quantity of the silicone in the emulsion is necessary to coat all the fibers in a fabric. Usually less than a two-percent increase in the dry weight of the fabric is required to encase the fibers with a silicone film only a few molecules in thickness. After the fabric is dried to remove water, it is given a short cure at temperatures of 250-300°F to polymerize this film of silicone oil to a tough, invisible sheath around the fibers. Under the influence of the curing temperature, some of the silicon-to-hydrogen bonds are oxidized to the very stable silicon-oxygen-silicon linkages. The silicone "skin" thus formed then becomes insoluble in both water and the common drycleaning solvents.

To show that the silicone skin exists and is continuous along each fiber,

* Presented at the Bismarck Hotel in Chicago, Ill.

Fortess of the American Celanese Corporation applied a silicone finish to acetate fabric in the usual manner. After the silicone had been insolubilized by curing, he dissolved away the acetate fibers with the solvent acetone. The silicone sheath around the fibers was not affected by the solvent. This is shown in Figure 2 by the microphotograph of the extraction residue. Note the continuous transparent skins of cured silicone that had surrounded each of the fibers.

CHEMICAL BASIS FOR PROTECTIVE ACTION———The earliest observed common property of silicones, as well as the organosilicon chemical compounds from which they are made, was that any surface contacted with them became water-repellent. First observed on glass flasks in their creator's laboratory, this behavior stimulated interest in the application of silicones as water-repellent fabric finishes. The organic groups attached to the silicone polymer orient themselves towards the outer surface of the silicone skin and act as protective sheaths, shedding water and water-borne soil that may contact the silicone-encased fibers (Figure 3). Oil and oil-borne soils, although they are not repelled by the silicone sheath and appear to wet its surface, are easily removed by drycleaning solvents. Oils and greases cannot pass through the impervious silicone film, which prevents them from being absorbed by the fibers in the fabric. Greases, oils, lipstick, cold cream and the other oil-like stains can easily and quickly be removed from a silicone-finished fabric with a sponge or a cloth dampened with cleaning fluid.

FUNCTIONAL SILICONE FINISHES———At first, interest was centered around rainwear, snowsuits and sports jackets of nylon and acetate because previous finishes were not durable to drycleaning solvents, whereas the silicone film, after curing, was not removed by solvents. Then interest shifted to other synthetic fabrics, particularly to those for women's suitings and light topcoating fabrics, when it was realized that silicone finishes offered not only durable water repellency, but resistance to spotting and soiling, a more permanent hand, better sewability, and other features which varied somewhat with the fabric construction.

HAND———Since the garment fabrics required a finish which could be varied to the hand customarily expected by buyers of the particular

Figure 2

Silicone skins from treated acetate fibers after solution of the acetate

fabrics, emulsions of at least four variants of the basic silicone finish had to be developed to produce hands variously described as soft, smooth and full, crisp and worsted-like, and crisp and full. This called for a bit more molecular engineering by our silicone chemists.

RESISTANCE TO SOIL———We have recently turned our attention to automotive-upholstery fabric because seat-cover manufacturers were finding our silicone finish satisfied the need of their customers for an automotive fabric that could be kept clean. When we contacted the automobile manufacturers, we found a whole new set of requirements. They wanted a fabric that could also be cleaned quickly on the assembly line from all the spots the factory men get on it during the assembly of an automobile. Too often an automobile must be pulled off the assembly line to be cleaned. Unfortunately, removal of these spots is in itself not sufficient; they must be removed without leaving a solvent ring. The ring caused by solvent spotting is a common phenomenon but is not clearly understood. It appears that particles of grit and dirt and some oils migrate with the solvent along the surface of the fabric and are then deposited in a ring when the solvent evaporates. Even the most tenancious of these oil-borne stains are now easily removed by the usual solvent-spotting methods from upholstery fabric properly finished with a new Dow Corning silicone finish designed for this purpose.

To meet these requirements of the automotive-production men, it was necessary to redesign the molecules on the outer surface of the silicone skin, so that there was less adherence to the silicone surface of greases and oils carrying dirt and grit. These soiling agents are thus more easily absorbed into a solvent-soaked cleaning cloth. This is shown by a photograph of both treated and untreated fabric cleaned of a lipstick stain. The solvent ring is completely eliminated on the treated fabric (Fig 4).

When we were satisfied we had the answer to a finish for automobile fabric, we were told we should also offer it for household upholstery. Automobile-fabric people pointed out that women buyers considering the upholstery and interior appointments of a new car were influenced subconsciously by their living-room furniture. Perhaps the opposite is also true. We contacted furniture makers and interior decorators and found that, here as in automobiles, the trend was to the new light shades, which milady wanted but didn't feel she could lightheartedly buy because they wouldn't be "practical," that is, one spill from a coffee cup and her expensive sofa would be ruined. Tests showed that fabrics treated with Syl-mer, as the new silicone finish was called, were easily cleaned. The fabrics felt smoother, wore better and stayed cleaner longer. As a consequence, many of the new lines of the outstanding furniture manufacturers feature Syl-mer-finished fabrics.

The development work done on the Syl-mer finish for upholstery fabric produced also a silicone molecule which could be cured with good efficiency at 250°F. Until this development, very little work had been done with the application of silicone finishes to wool because the usual curing temperatures near 300°F were much too high for the satisfactory handling of wool fabrics. With the advent of the faster-curing silicone and improved catalysts, a finish, designated Dow Corning 105, was designed especially for wool to cure at 250°F. For example, a 14-oz suiting can be cured in 7 to 10 minutes at this temperature. This finish produces a full hand and on some fabrics gives the impression of increased thickness and fullness. Initial spray ratings of 100 are easily obtained even on fabrics having considerable nap.

WEAR RESISTANCE FOR WOOL ———Tensile-strength and abrasion tests are of prime interest on treated fabric. Limited work has shown encouraging results, and this testing program is being carried on until a

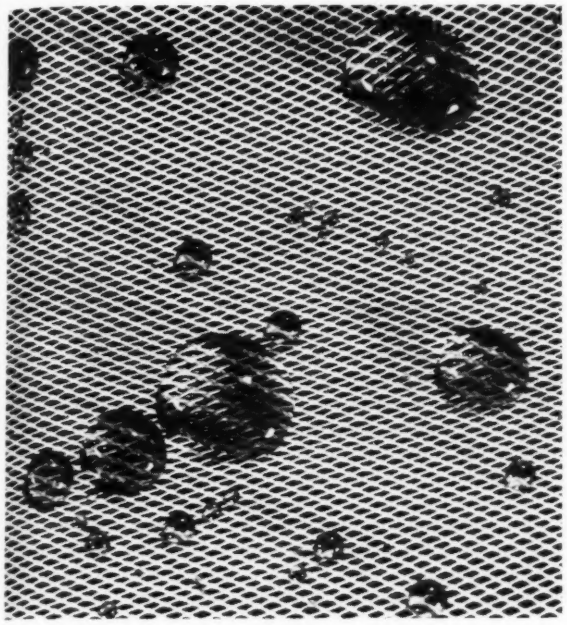

Figure 3
Water-repellent silicone-treated fabric

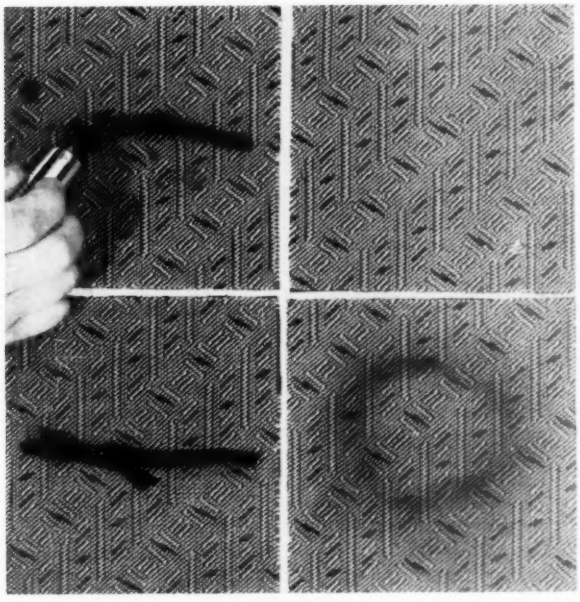

Figure 4
Complete removal of stain (upper right) from silicone-treated fabric

wide variety of constructions containing several grades of wool have been thoroughly investigated, so that performance can be accurately predicted. Table I lists some typical flex-abrasion-resistance results on treated and untreated wools. Tensile strength data obtained to date show no significant improvement in the treated fabric, but the original values are maintained in almost every case, and this is an important factor to be noted. By virtue of the water repellency imparted to the fiber, there is a definite improvement in the ability of the fabric to maintain a crease or press under humid or wet conditions.

REDUCTION OF FELTING SHRINKAGE———For several years we have thought the presence of a silicone polymer which encased the fibers in a wool fabric could be used to decrease the felting shrinkage of such a fabric during laundering. Considerable progress can be reported at this time.

Dow Corning 112 emulsion has been especially formulated to reduce felting shrinkage, although it also produces a desirable hand, durable water repellency and the stain resistance associated with the other silicone finishes. It is applied with a catalyst, so that 3-5% silicone solids are deposited on the fiber, followed by drying and curing at 250°F. The length of curing time will vary with the weight and construction of the fabric, although it is usually 8-15 minutes.

TABLE I
CSI STOLL FLEX-ABRASION TESTS OF WOOL FABRICS TREATED WITH DOW CORNING 105

Type of Fabric	Average Values in Warp Direction	
	Untreated	Treated
Gabardine	1396	2674
Flannel	640	862
Covert	1493	1856
Uniform fabric	3304	3741

Table II shows typical data obtained on woolen blanket and worsted suiting fabrics.

Work with wool blends has shown similarly satisfactory results if the wool content is above 50%. With percentages lower than this, very little stabilization results.

The Dow Corning 112 finishing process for wool seems to offer several advantages. The application procedure is simple, only a pad or quetch and standard drying and curing equipment being used. Extensive instrumentation or chemical control is not required. The process is carried out just prior to final finishing. No afterwashing or softening is required and the normal napping, shearing and decatizing can be carried out on the treated fabrics. The strength of the treated fabric appears to be unchanged, although a slight increase in flex abrasion has been noted. Laboratory work is being continued to increase the efficiency of the treatment and to reduce the amount of finish required for acceptable shrinkage control. Further research is also being devoted to accelerate the polymerization rate of the silicone so that the process can be more conveniently fitted into a normal production schedule.

NEW METHOD OF APPLICATION———In many woolen or worsted mills we find it difficult or impossible to apply silicone finishes. A

TABLE II
FELTING RESISTANCE OF WOOL TREATED WITH DOW CORNING 112

Fabric	Relaxation Shrinkage	Total Shrinkage 1st Wash	Total Shrinkage 10th	Actual Total Felting
	%	%	%	%
Treated Blanket warp	3.4	5.0	5.4	2.0
fill	0.6	0.0	0.4	0.4
Untreated Blanket warp	4.2	18.8	18.7	14.5
fill	1.3	14.2	14.0	12.7
Treated Suiting warp	2.9	3.4	6.2	3.3
fill	2.0	1.7	4.5	2.5
Untreated Suiting warp	3.8	9.6	25.1	21.3
fill	3.4	5.5	18.9	15.5

large number of these mills do not have adequate padding equipment or drying ranges capable of curing the finish economically. To assist these mills in obtaining the maximum values of silicones, we have recently prepared a silicone emulsion and catalyst which can be applied by the exhausting method. By balancing the electro-potential of the silicone emulsion-catalyst combination to that of fabrics containing a minimum of 85% wool, chemist have engineered a finish that is selectively adsorbed onto wool fiber. Exhaustion is complete to the extent of 95% in 30 minutes at temperatures less than 100°F. A dyebeck or dolly washer would normally be used to apply the silicone in these mills. Ordinary drying temperatures are sufficient to develop durable properties such as water repellency with this finish.

ADDITIVES TO RESIN FINISHES ——The recent increases in the use of synthetic resins in fabric finishing particularly in the field of minimum care cottons has created an entirely new field for silicones. Engineers have known for some time that certain of methyl and phenyl substituted siloxanes are highly efficient lubricants for plastic surfaces. Using this knowledge our textile research chemists have formulated silicone lubricants to be used in low concentrations as adjuncts to resin finishes. For this purpose water repellency is not necessary and often undesirable. The principal properties sought are improved tear strength and sewability of the finished fabric and reduced tackiness during the application of thermoplastic resins. These properties must be as durable to laundering as are the resins used in the finish.

The problems involved in formulating a silicone for this purpose were two-fold. The silicone had to be made into a stable emulsion which would be compatible with a great majority of the resin formulations being used. The more difficult problem was one of designing a silicone which would polymerize at the usual resin curing temperatures to a soft plastic film rather than a brittle resin-like material.

Magic Skin ——

(*Concluded from page P376*)

glory and profits. But, when we went to the mill a week later for the decision we were presented with charts showing that the average cost of dyestuff per yard was 1¢ and that the cost of glycerine plus the cost of padding and drying was worth ¼¢. Since the average increase in color value could be expected to be 25% or exactly ¼¢, there was no sense going through the procedure. However, if there are any printers present, take note that, if you want penetration of 50% to 75% color value on the back of the cloth, then this procedure may still be practical. Did this failure shrink our skin? Plenty! We rubbed the skin of research, made our wish, but there were no profits.

Then came shrinkproofing—one process for rayon and blends, the Definized Process, and another for wool, the Protonized Process. So important was the development for shrinkproofing of rayon and so successful were the results that American Viscose Company had four of their textile engineers follow our work at all demonstrations for months, and finally they took it upon themselves to announce the process to the trade. Arthur Wachter, of American Viscose Company, gave a dramatic speech in New York to several hundred textile technologists announcing that our process and Cluett Peabody's Sanfoset were the final solution to the old problem of stabilizing rayon to washing. The papers carried the news the next day, and pandemonium let loose in our office. We had phone calls, wires, cables, asking for a demonstration of our process. Many millions of yards were successfully stabilized, licenses were signed by 12 mills, and yet it was a complete failure. Did our skin shrink? Plenty! And so did our assets. Reasons for failure; what were they? Remember the gray market in caustic? Well, that was the year we brought out the rayon shrinkproofing process. The next year, when caustic became freer, there was a gray market in textiles. Anything sold—no shrinkproofing was needed. And, the final coup de grace was administered to the process when the demand for crushproofing became more important than shrinkproofing. The resins, although giving poorer washfastness, plenty of chlorine retention, and not much crushproofing, won out. The treatment of rayon with 40% caustic is the best process ever devised for shrinkproofing and yet was a failure. Net result: $200,000 spent in research, sales, and promotion; return, $3000 in royalties. The moral of all this is that textile chemical specialty manufacturers should stick to chemical manufacturing and leave process development to the textile mills, unless they have a chemical to go along with the process, such as, for example, Zelan or crush-proofing.

TRENDS

A word about the trend in the textile chemical specialty business. More and more emphasis is being placed on research. The specialty manufacturer is faced with constant change in fiber and fabric, in styles from soft to crisp and in between; difference in demand from mill to mill. The synthetic fibers present all kinds of processing problems in dyeing and finishing. The newer and growing specialties are the silicone resins; thermoplastic resin for wash and wear; improved cationics, particularly regarding solubility and nonyellowing; products to make direct dyes fast to soap washes; the old standbys—flameproofing, mildewproofing, and a nonnitrogenous, nonchlorine retentive resin for crushproofing. I venture to say that as much money has been spent on flameproofing over the past 400 years as was spent on the development of atomic energy.

CONCLUSION

Let me conclude my rambling remarks with an appeal for sympathy for the textile chemical specialty manufacturer and, particularly, for his salesmen. Remember that he and his salesmen are an integral part of your industry and try their best to serve you. Extend your sympathy to the salesman's wife and family also, for he works hard, travels much, and is lucky to see his family on weekends. Welcome him to your office, for no matter how troubled and harassed you may be, he will cheer you up not only with his ready cures for your processing problems but also with the Rabelaisian stories he will tell you at the drop of a hat. Remember also that your monthly dinner meetings and your yearly conventions would be dull affairs, indeed, without his presence and the gifts of Bacchus he dispenses with such abandon and generosity.

LITERATURE CITED

(1) Philip, R W, *Ind Eng Chem*, March, 1955.
(2) *America's Textile Reporter.*

Niagara Frontier Section ——

FACTORS INFLUENCING THE SUCCESSFUL APPLICATION OF DIRECT DYES*

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General Dyestuff Co
A Sales Division of General Aniline & Film Corp

INTRODUCTION

IN the past ten years there has been a tremendous amount of work done in the investigation of the dyeing properties of direct dyestuffs when applied to cotton and rayon. Among those who have been instrumental in leading the way to make possible the vast amount of dyeing behavior data that is available today, the names of Boulton, Whittaker, Lemin, Vickers and Vickerstaff are probably the most outstanding. For the production of level, well-penetrated dyeings on cotton or rayon, it is generally accepted at the present time that the most important factors governing the choice of dyestuff with respect to dyeing behavior are 1) its level dyeing or migration power and 2) its salt controllability.

No matter how much information the dyestuff manufacturers incorporate into their pattern cards and circulars concerning the dyeing behavior of their products, there will always be a certain amount of difficulty encountered in the dyehouse either from limitations imposed by fastness properties, dyeing costs, or even improper handling of salt and temperature controls at the dyehouse level. It is our purpose therefore to attempt to indicate some of the practical aspects of the available dyeing behavior data for direct dyestuffs and other factors directly related to this problem.

The art of direct color dyeing has long been a fairly well-established procedure, and because of the apparent ease of the process it has generally been considered that little control is necessary to obtain satisfactory results. However twenty years research into the nature of direct dyeing on cotton and rayon has proven that in many direct dyed combinations careful control of salt additions and temperature may be necessary for perfect results.

E M Taylor

A brief outline of the theory of dyeing cellulosic fibers with direct colors is presented and the important part that common salt plays in direct color dyeing is explained. Factors that the dyer must consider in practical application with respect to rate of absorption and dyeing behavior are discussed. The effect of temperature, liquor ratio, circulation and the presence of electrolytes is given. Classification of direct dyes into classes A, B, and C, according to dyeing behavior and an indication of how to handle each class is explained.

The reduction of direct dyes and the effect of hard water in relation to dyeing behavior is discussed. Emphasis is placed on proper dyestuffs selection as related to fastness and dyeing properties.

THEORY OF DIRECT DYEING

In order to give some background to an understanding of dyeing behavior, I would like to discuss briefly in a simplified form the theory of rayon dyeing as set forth by Boulton (*1*), which in essentials is applicable to other classes of dyes and other fibers.

Viscose rayon, like other textile fibers, is made of polymeric chains packed together to form filaments, and while the molecular packing is not uniform throughout the fiber, these chains lie roughly parallel to the fiber axis. When a filament is wetted, water is strongly absorbed, and pushes aside the disordered chains in the amorphous parts, creating pores in the structure. The dye molecules thus enter and pass along the water filled channels by diffusion. The rate of diffusion of direct dyestuffs into the fiber is a property which varies probably more between individual dyestuffs than any other property.

Direct dyestuffs are almost invariably long-chain structures comprising aromatic azo compounds which contain several substituent sulpho groups to make them water soluble, and the dyes themselves usually are sodium salts of the sulfonic acids. We now come to a point where the tremendous importance of common salt in direct color dyeing can be explained. Direct dyestuffs in solution behave as colloidal electrolytes. By this we mean that the dyestuff will exhibit such colloidal properties as gelling, salting out and thixotropy and at the same time behave like electrolytes showing the properties of ionization and the conduction of electrical current. Because of their colloidal properties, dyes in solution are affected by changes in temperature and the presence of other electrolytes. When common salt, which is a strong electrolyte, is added to a solution of dyestuff, it increases the degree of aggregation of the tiny dispersed particles which result when the dyestuff is ionized in solution.

Viscose rayon filament carries a negative electrical charge on its surface. Dyestuff anions are also negatively charged, and because of the fact that like charges repel each other a pure dyestuff, containing no electrolyte in the form of diluent, applied in distilled water will show practically no affinity to a pure cellulosic fiber. The first effect of an electrolyte therefore is to overcome the repulsive force between the dye and the fiber surface, and thereafter the additions of further quantities of salt have the effect of lowering the solubility of the dye and shifting the equilibrium absorption in favor of the absorbing fiber. Therefore the use of salt for direct dyeing is essential to promote exhaustion of the dyestuff onto the fiber.

We have already seen in the ionization of the dyestuff that salt aggre-

* Presented before the Niagara Frontier Section on January 20, 1956 at the Park Lane Restaurant, Buffalo, N Y.

gates the dye dispersion and this fact is of great practical importance. The first stage in dyeing is the contact between dye aggregates and fiber surface, and if the aggregates are small enough to diffuse into the fiber, the smaller aggregates become absorbed and the larger ones gradually break down. If too much salt is present and the aggregate grows rapidly, there is an accumulation of relatively insoluble dye near or on the fiber surface and because the large aggregate cannot diffuse properly, we have on the most accessible surface of the material a somewhat heavier layer of dye salted on. This is commonly referred to as a "bad strike" and indicates a dyeing which has started wrongly and one which only time and excessive care will rectify.

Finally once inside the pores, the dye molecules diffuse throughout the fiber and by means of a cohesive force known as hydrogen bonding, the dye becomes fixed by the formation of a bonded complex with cellulose chain molecules in the inter-structure of the fiber. This is made possible because there are either some azo, amino, phenol, or amide groups present in the dyestuff capable of hydrogen bonding with the hydroxyl groups of cellulose. In time an equilibrium between the dye solution and fiber is reached at which the concentration of dye between the bath and the dyed material becomes constant. This effect takes place under conditions of constant temperature and dyebath concentration.

VARIABLES INFLUENCING DYEING PROCESS

However, in actual dyehouse procedure the dyer does not work under constant conditions, nor does he dye to equilibrium. Because he has a definite shade to match in a more or less reasonable amount of time, additions of dyestuff and salt may be made periodically, the temperature of the dyebath may be varied and even the quantity of dye liquor varied. Thus other important factors are involved that influence the end results.

TEMPERATURE———The first of these variables to be considered is temperature. Increasing the temperature of the dyebath increases the rate of diffusion of the dye into the fiber and thus leads to a more rapid leveling out of the initial non-uniform strike of the color. A further effect of an increase in temperature is to lower the amount of dye absorbed at equilibrium. We will discuss in a following paragraph how temperature control of a dyebath may be employed to achieve successful results when using a difficult dyeing type of direct color.

LIQUOR RATIO AND CIRCULATION———The second variable is liquor ratio and degree of circulation. In a short liquor ratio where the relative concentration of the dyebath is increased, the effect is to increase the rate of dyeing and the amount of dye absorbed on the fiber. As the dyer has less control over the exhaustion when working in a short liquor ratio, a greater degree of care must be exercised. The degree of circulation in the dyebath with respect to the fiber will have some effect on the distribution of the dye in the fiber. An increase in circulation or agitation assists in obtaining a more uniform strike throughout the mass during the initial distribution of dye.

DYEING PROPERTIES———The third variable influencing the dyeing procedure is the behavior of the dyestuff with respect to salt sensitivity and level dyeing. Based on their level dyeing and their salt controllability all direct dyestuffs can be classified into three groups as follows (*2*):

Class A—Dyes possessing good level dyeing properties.

Class B—Dyes possessing poor level dyeing properties but whose exhaustion can be controlled by proper addition of salt.

Class C—Dyes of poor leveling properties and high rate of exhaust which require both temperature and salt control.

A dyestuff in Class A is probably a rapidly diffusing dye and may show a relatively high exhaust in the absence of additional salt. It will be rapidly exhausted from the dyebath and will penetrate and level readily, whether sensitive to salt or not. Dyestuffs in this class offer no particular difficulties in application and the additions of salt do not need to be so rigidly controlled.

Class B dyestuffs diffuse fairly slowly, exhaust gradually as the dye diffuses into the fiber and have a slower leveling capacity than dyes in Class A. While these dyestuffs do not level well, the production of even dyeings is facilitated by the gradual addition of salt.

In order to obtain an even result with Class C dyestuffs, salt must be added with extreme caution, and in addition it becomes necessary to regulate the temperature of the dyebath. The problem here is to reduce the rate of exhaustion so that the dye liquor does not become highly exhausted until there has been time for all parts of the material to be in contact with it for an appreciable time. Two methods are available for control: 1) start the dyeing without salt and exhaust the bath by gradual additions of small increments of salt, or 2) reduce the temperature of dyeing in the early stages. Temperature control without salt control is of little value in obtaining satisfactory results.

The manner in which the salt is added is an extremely important factor in direct color dyeing, especially when using Class B and Class C dyestuffs. The first two or three additions of salt are the most critical and the quantities employed here have a considerable bearing on the final results. The first addition of salt to the dyebath should be not more than ⅛-¼% owf. Subsequent additions several minutes apart can be made in increasing quantities, each one double the preceding amount, eg, ¼%, ½%, 1%, 2%, etc, until the required amount of salt for the depth of shade being dyed has been added.

The usefulness of this classification in dyeing shades with single dyestuffs is quite evident. The class into which the chosen dye falls immediately indicates the best suitable dyeing method for obtaining level results. With respect to selecting dyes for combination shades, one cannot accurately predict that compatible combinations can be selected on this classification basis, as the presence of a second or third dyestuff may appreciably alter the individual dyeing behavior of the components. It is suggested that, if at all possible, the dyes in a mixture should fall in the same class, but on the other hand certain requirements of light or washfastness or dischargeability may necessitate using dyestuffs of different classes.

In mixing dyestuffs of different classes, the choice of dye method should be governed by the dye which is most difficult to apply. If the only requirement to be met by a dyer was turning out a well-penetrated, level piece of goods, he would undoubtedly stock his drugroom with Class A dyestuffs only and then sit back and relax. However, with the present trend toward increased light and washfastness the dyer's problem becomes more acute. The very level dyeing colors in Class A are generally those that exhibit the lowest degree of wetfastness, so that with the possible exception of pastel shades the use of this

class of dyes is limited to end usages where there are no particular demands for wetfastness. When it comes to lightfastness there are many Class A dyestuffs that possess very good properties.

The great majority of the direct dyestuffs that possess the best fastness to light and washing are in Class B and C, so that an increase in fastness requirements usually indicates a greater need for application control in the dyehouse. It becomes necessary therefore that when the dyer chooses his formulation to match a given dyeshade, he considers the dyeing behavior of his components as carefully as he does their relative fastness properties. In this connection I would like to state that as our substantive color cards are revised and reissued we are including such pertinent data to assist the dyer in the best choice of dyestuffs to do his particular job as satisfactorily as possible.

Although the requirements for successful cotton dyeing are not so exacting as they are for rayon because of the generally lower initial strike and the slower rate of absorption, the same classification of dyestuffs and control methods apply to this fiber. Mercerized cotton yarns and piece goods will naturally require much more control than unmercerized goods, and if the new cyanoethylated cotton fiber becomes accepted on a practical scale probably even greater difficulties are ahead for the dyer. While we have not made a thorough investigation into the dyeing behavior of this fiber toward direct colors, work that we have done to date indicates that both the initial strike and the rate of absorption of direct dye by cyanoethylated cotton appear to be very high. Possibly as much or even greater control of salt and temperature, in comparison with rayon, may be required for the successful dyeing of this modified cellulose form.

Due to the limitations of time it is not possible to broaden the subject of dyestuff classification into a discussion of application methods in relation to the different dyeing systems used for yarns and piece goods. However, in the future we hope to be able to go into this subject further.

REDUCTION

Another factor important in the successful application of direct dyestuffs is the sensitivity of some colors to reduction in the dyebath. This phenomenon has been the cause on more than one occasion of complaints being received by dyestuff manufacturers for supposedly off-shade or weak material.

Reduction difficulties are apt to be met more often when dyeings are made in closed systems such as package machines or enclosed jigs or overhead reels than in open jigs, kettles or skein dyeing equipment. Dye reduction may show up as a change in hue, either slightly or in some cases to a completely different color, or as a loss in depth. Here again the amount may be small, but in some cases it has been known to be severe enough to cause complete discoloration of the dyestuff.

The reduction of direct dyes during the dyeing of cotton or rayon is due to the fact that cellulose in hot alkaline solution (*3*) forms a reducing system strong enough to affect certain colors. With cotton this reduction in alkaline solution is accelerated by the presence of the starches and pectins that are found in the natural cellulosic fiber. Since the normal dyeing process involves the use of material, dye, water, salt and a dyeing assistant, one or more of these has to be the source of alkali. Incomplete scouring or desizing of cotton material, carry-over of alkaline scouring materials into the dyebath, carry-over of boiler-house additives to the dyehouse steam lines, high pH of the water used for dyeing, and alkaline diluents used in the standardization of the direct dyestuff are all potential sources of trouble. Sometimes it is difficult when dyeing combination shades to pick out the offender. For example, a dyestuff which is susceptible to reduction that contains no alkali as a standardizing agent may work satisfactorily when used as a self-shade. However, if used in combination with a dye standardized with an alkali the first dyestuff would be affected.

The most satisfactory way of overcoming dye reduction appears to be control of the pH of the dyebath, and this can be done very effectively by the addition of 2-5% Vegan Salt A owf to the dyebath. The quantity of Vegan Salt A varies according to the amount of alkali present and also the time and temperature of dyeing.

HARD WATER

The third and final point that I would like to discuss briefly is the effect of hard water on some direct dyestuffs, especially in relationship to their classification in groups A, B and C according to their dyeing behavior. Although many textile establishments have some sort of water softening system in their plants or depend on municipally softened water for their dyeing operations, there are still a large number of mills dependent on unsoftened natural sources of water. Even in plants where some attempt is made to keep hardness within a tolerable limit, occasions may arise where the system may get out of balance due to breakdown, seasonal variations of source of supply, or excessive demand. Where there is a water softening process a partial solution to the problem will be obtained, but much depends on the type of water and the method of softening adopted. Some softened water will develop alkali on boiling and this, in turn, leads to the danger of dye reduction as previously described. In an earlier part of this paper we have seen the effect of an electrolyte on a solution of direct dyestuff, how it has the property of aggregating the dye particles. Calcium and magnesium salts are considerably more powerful in their aggregating properties than sodium salts. Campbell dyeing of Chlorantine Fast Blue GLL (*4*) has found for example that on a 200% used as a reference type for dyes so sensitive to large amounts of electrolytes that in the absence of added sodium chloride they give a heavy "strike," calcium and magnesium salts were four times more powerful in "striking" power than sodium salts. This is attributed to the increased "salting on" power of the bivalent calcium and magnesium ions compared with the univalent sodium ion.

In addition to these dyestuffs that show a much greater initial strike, there are a large number that are insoluble in or precipitated by hard water at the boil. These dyestuffs will ordinarily yield shades of very weak tinctorial strength even upon addition of common salt to the bath. A good example of this latter group is the well known Brown BRL (Pr 47) type.

Another difficulty resulting from the presence of calcium and magnesium salts is that many of the Class B dyes, especially those that may be borderline cases become Class C dyes when dyed in hard water.

To overcome the objectionable quantities of calcium and magnesium salts in hard water it is necessary therefore to use a sequestering agent of some type in the dyebath. One must be careful in the choice of sequestering agent, however, because our laboratory tests have shown that sequestrants based on the tetrasodium salts of ethylene diamine tetraacetic acid which have become widely accepted in the textile industry cannot be used in a dyebath containing a metal com-

plex direct dyestuff. The sequestering agent sequesters the copper from the molecule of the dye and in most cases an appreciably weaker shade of much poorer lightfastness is obtained.

Sequestering agents of this general chemical structure can be safely employed in dyebaths containing copper free dyestuffs. Where the metal complex types of generally high lightfastness are used, an addition of 4-6 oz of sodium metaphosphate per 100 gals of dye liquor, depending on the degree of hardness, should be adequate to prevent precipitation of the dyestuff and reduce the initial strike of the dyestuff.

SUMMARY

In this short discussion we have attempted to bring out some of the most important factors that determine the success or failure of direct color dyeing. In conclusion it bears repeating once again, that a knowledge of the dyeing behavior and dyeing characteristics of a dye is just as necessary as a knowledge of its fastness properties.

REFERENCES

(1) Boulton, *J Soc Dyers Col* **67**, 522 (1951).
(2) *Ibid* **62**, 280-5 (1946); **64**, 145-6 (1948).
(3) Wilcock, *ibid* **63**, 136 (1947).
(4) Campbell, *ibid* **66**, 120 (1950).

Activities of the Local Sections

LADIES NIGHT — **PHILADELPHIA SECTION** — **APRIL 20, 1956**

"The Yarn Behind Fabrics of Fashion"

(*See pages P342-3 of previous issue*)

DRESSES AND COSTUMES

A—Abe Schrader	Two-piece Promenade ensemble personified in color	Fabrex
B—Pauline Trigere	Exclusively knit, fast color with papoose for informal wear	Jasco
C—Malcolm Charles	A lustrous silk and cotton in Champagne for Tea Time	Onondaga
D—Oleg Cassini	Empire line, sleeveless, colorful and dramatic cocktail dress	Hopkins
E—Martini	Black shoulder strap sheath in "Silcotta," striped jacket for after-five	Fabrex
F—Pauline Trigere	Embroidered cotton with Jacquard patterning two-piece dress, noon to dark	Staron
G—Oleg Cassini	Black sheath trimmed with Toast of lustrous cotton knit, smart look	Hopkins
J—Martier-Raymond	Three-piece ensemble in Aberfoyle's Donpioni cotton	

SUITS

E—Lady Renlyn	A new yarn, colorfully designed in a two-piece suit	Chalet
M—Elfreda	Miniature black/white checked two-piece suit for travel	Elgin

JUNIORS

N—Mr MORT	Date-for-Spring dress in a bouffant Aberfoyle cotton	Chantilly
O—Ira Rentner	Gay, colorful, airy silk and cotton flared skirt dress	Stehli

SPORTSWEAR

P—Catalina	Swimsuit of Aberlon, an exclusive Orlon by Aberfoyle	Catalina of Aberlon
Q—Catalina	Chic, trim swimwear, an exclusive cotton	Catalina of Aberfoyle cotton

MENSWEAR

K—House of Worsted-Tex	"Silcotta" in a distinguished gentleman's business suit	Fabrex
I—Haspel	New summer wear of Aberfoyle's Type "63" Dacron and cotton	Earl-Loom
R—Van Heusen	Silk and cotton colorful sport shirt for casual living	Parliament

CHILDREN'S WEAR

L—Savoy	Exclusively knit fabrics for children, designed for comfort	Savoy

COATS

S—Lassie Junior	Reversible colorful coats, Spring to Summer for a graceful wardrobe	Fabrex

Hats courtesy of: B F Dewees, Philadelphia

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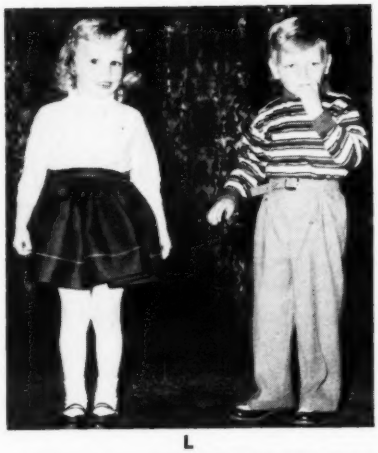

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Pacific Southwest

FORTY members and guests were present at the most recent quarterly meeting of the Pacific Southwest Section on April 27th in the Public Relations Office of Western Carloading Co, Los Angeles, Calif.

Highlight of the meeting was the showing of a color film "Arts and Crafts in China" by Rupert Sewelson, president of Carpet Crafts Inc.

Melville H Behrendt, chairman of the Outing Committee, announced the availability of the Ojai Valley Inn or Rancho Sante Fe for the 1956 outing. He will survey the membership by letter.

Progress on the Section's 1956 Intersectional Contest Paper continues, with materials and exposure boxes having been secured for tests. PSW plans to present a paper entitled "Report on the Effect of Smog on Textile Materials in Los Angeles" at the 1956 Contest. Members of the Committee include: Thomas P Lee, *chairman*, Fred Ahl, Rita Landry, Paul Noonan, Robert Sumers, and Fred Wigglesworth.

In lieu of a dinner charge, contributions were collected from the members present. This, plus monies collected from miscellaneous sources, is to be used for a fund from which a library of technical books is to be purchased. The library will be maintained by the secretary, Clarice H Lindsey. A committee will be appointed to administer the fund.

The next quarterly meeting is scheduled for June 22.

AATCC Calendar

COUNCIL
June 15 (New York); week of Sept 10th (New York, N Y); Nov 16; Jan 18, 1957

NATIONAL CONVENTIONS
Sept 13-15, 1956 (Waldorf-Astoria, New York) (as part of the Perkin Centennial, Sept 10-15); 1957 (Boston); 1958 (Hotel Conrad Hilton, Chicago); 1959 (Washington, D C)

HUDSON-MOHAWK SECTION
June 22 (Annual Outing)

MID-WEST SECTION
June 16 (Outing—Browns Lake Resort, Burlington, Wis)

NEW YORK SECTION
June 22 (Outing—North Jersey Country Club, Wayne Township, N J)

NORTHERN NEW ENGLAND SECTION
Sept 28 (Annual Outing—Wachusett Country Club, West Boylston, Mass); Oct 19 (Science Park, Boston, Mass); Dec 1 (Annual Meeting—Hotel Vendome, Boston)

PHILADELPHIA SECTION
Sept 28 (Abraham Lincoln Hotel, Reading, Pa); Nov 2 (Drake Hotel, Philadelphia, Pa); Dec 7 (Kugler's Restaurant, Philadelphia, Pa)

PIEDMONT SECTION
June 8-9 (Outing—Mayview Manor, Blowing Rock, N C); Oct 6 (Annual Meeting—Hotel Charlotte, Charlotte, N C)

RHODE ISLAND SECTION
June 15 (Annual Outing, Pawtucket Country Club); Oct 18 (Johnson's Hummocks Grille); Dec 6 (Annual Meeting, Johnson's Hummocks Grille)

SOUTH CENTRAL SECTION
June 22-23 (Lookout Mountain Hotel, Chattanooga, Tenn); Dec 1 Hotel Patten, Chattanooga, Tenn)

SOUTHEASTERN SECTION
June 8-9 (Outing—Radium Springs, Albany, Ga); Sept 22 (Columbus, Ga); Dec 8 (Atlanta, Ga)

WESTERN NEW ENGLAND SECTION
June 15 Outing—Wallingford Country Club, Wallingford, Conn); Oct 15 (Annual Meeting—Hartford, Conn); Nov 16 (Rapp's Restaurant, Shelton, Conn)

Hudson-Mohawk

THE Hudson-Mohawk Section held its annual Ladies Night at Schuyler Meadows Country Club, Albany, N Y, on Friday, May 18, at which time William A Nelson of Ritter Chemical Co was awarded the Dr Jack Epelberg Award for meritorious service to the Section during the past year.

The occasion also marked the annual election of officers. Those elected for the coming year are: *Chairman*—Albert E Herrmann, Jr, General Aniline & Film Corp; *Vice chairman*—Edward A Chevrette, Apex Chemical Co; *Secretary*—Maurice Fishman, Lee Dyeing Co; *Treasurer*—John W Merrill, Cluett Peabody & Co.

New York

THE annual ladies' night meeting of the New York Section was held on Friday evening, May 18th, at Kohler's Swiss Chalet, Rochelle Park, N J. Miss Hazel Bishop, cosmetic chemist, discussed the "Philosophy of Cosmetics." The following officers were elected: Donald E Marnon, *Chairman;* John A Komninos, *Vice Chairman;* Richard P Monsaert, Jr, *Secretary;* and Richard E Miller, *Treasurer.* Dancing followed the meeting.

The annual outing of the Section will be held June 22nd at the North Jersey Country Club, Wayne Township, N J, under the chairmanship of Robert Brewer.

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May 18, 1956

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Frederick Best—Lab tech, supervisor of colorfastness lab, Celanese Corp of America, Summit, N J. Sponsors: F Fortess, V S Salvin

Walter J Boshart—Chemist, Celanese Corp of America, Summit, N J. Sponsors: D B Thornton, F Fortess

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Tommy Zau — Bradford Durfee Technical Institute. Sponsor: J Watters

APPLICATION FOR TRANSFER TO SENIOR MEMBERSHIP

William S Barnard

Thomas Carter

Perkin Centennial Notes

KODAK EXHIBIT AT GRAND CENTRAL TERMINAL TO SHOW APPLICATIONS OF COLOR PHOTOGRAPHY IN "MORE COLORFUL" WORLD

WHEN the Perkin Centennial is celebrated September 10 to 15, the world-famous Kodak Photographic Information Center in New York City's Grand Central Terminal will be devoted to an exhibit showing the application of modern color photography in the "more colorful world" of today and tomorrow.

On display, too, will be products illustrating the use of dyes in the manufacture of the newest in modern plastics and the nation's latest textile fibers.

As such—along with the great Kodak Colorama—the exhibit is expected to prove one of the major focal points of a centennial celebration which will pay tribute to the man who first synthesized color dyes.

Part of the display will be presented as a color slide show, operating continuously from 10 to 10 daily, to depict the chemical and physical nature of the layers of photographic emulsion on a typical color film and the manner in which dyes are formed in the emulsion by the photographic developing process.

The slide show will thus illustrate the layering of the emulsions, the components of each layer, the action of the layers and their components when exposed to light and processed, and the final result. The slides will also depict what this process means to people everywhere, not only from the personal standpoint but as a means of producing photographs with many applications in business and industry, science and medicine, education and commerce.

In addition, Kodak is planning two pairs of contrasting oversize color transparencies which will demonstrate that before the modern utilization of synthetics, color was the privilege of the few, whereas today it is the pleasure of the many.

The first of the contrasting transparency pairs (each picture being 30 by 40 inches in size) will depict an historic figure garbed in royal purpose contrasted with the brightly colorful and casual dress of today's teen-agers. The second pair will contrast the comparatively dull and drab household of the Victorian era with the brilliantly colorful decorative scheme of contemporary homes.

Also on exhibit at the Kodak Center will be materials showing the results that can be achieved from amateur color films. These range from full color photographic prints on paper to color slides and enlargement suitable for decorative use in the home.

Also, exhibit space will be devoted to a display featuring the role of color in modern fabrics and plastics.

Concurrently Kodak's photographic print show at the Information Center will be devoted to a major display of outstanding color photographs produced by the Kodak Dye-Transfer Process. These prints made from photographs shot by the staff of *Sports Illustrated* magazine, in addition to being brilliantly colorful, will consist of some of the most dramatic sports color photographs of the last several years.

Finally, at the exhibit behind the Colorama, Kodak will have a display of the latest in miniature cameras and picture-taking aids—all specifically intended for fine color photography.

The culmination of the entire Kodak exhibit will, however, be the giant Kodak Colorama itself. This spectacular color transparency is a full 18 by 60 feet in size, and is made by direct enlargement from a color negative onto color transparency film, resulting in the "largest color pictures in the world."

During the Perkin Centennial the picture in the Colorama will be a spectacular color photograph of Water Wheel Falls in Yosemite National Park, California. Photographed from a hillside overlooking the fiercely tumultuous white water, the picture not only captures the beauty of one of America's most scenic spots—but also the full, delicate color of a graceful rainbow arching above the river.

Patent Digest ——

(*Concluded from page 364*)

to form a ring structure of the type of maleic anhydride, succinic anhydride, alkylene carbonates and the like.

Brit Pat 568,092 (Tootal Broadhurst Lee Co/1945): pretreatment of nylon with strong inorganic acids to obtain deeper dyeings.

Brit Pat 584,758 (British Celanese/1947): increased color depth of nylon is attained by adding a swelling agent (phenol, etc) and a lower alcohol to the dyebath.

DYEING ACRYLONITRILE FIBERS——Cuprous-Ion Technique Using Furfural

C,4,07

USPat 2,700,589 (Du Pont——Iannarone——Jan 25, 1955)

The cuprous-ion technique for dyeing acrylonitrile homo- or copolymer fibers has been widely adopted. Reference may be made to USPat 2,653,-074 (Du Pont-Blaker/1953) [cf *Am Dyestuff Reptr* 43, 383 (1954)], which advocates the use of hydroxylamine as a reducing agent to transform cupric in cuprous ions.

The current specification indicates that metallic copper might easily be precipitated in working with standard reducing agents, such as sodium- or zinc sulfoxylateformaldehyde, especially when short baths are used. On the other hand, the cuprous ion formed may be reoxidized to the cupric ion by the oxygen in the air when longer baths are employed.

It has been observed that strong and level dyeings are obtained with acid wool dyes using the cuprous-ion technique on the above material by applying furfural as a reducing agent. The dyeing temperature has to be at least 222°F, and, according to the examples, between 225 and 250°F. The best pH range is within 1.5-5.0 and preferably from 1.5-3.0. Solutions of lower pH values are apt to corrode the equipment, while higher pH produces duller shades. The higher temperatures (240-250°F) are particularly advisable for the dyeing of highly drawn fibers. Color absorption of this material is low around 212°F, while temperatures above 250° cause excessive shrinkage.

Example: a package of polyacrylonitrile sewing thread, drawn to 8 times its original length, is dyed in a circulating machine adapted for pressure dyeing with 1.5% of the acid wool dye Pontacyl Fast Red AS Ex Conc (*CI* 176), 10% furfural, 6% copper sulfate-pentahydrate and 5% sulfuric acid. Furfural first and then the sulfuric acid is added to the copper sulfate solution. Upon the addition of some more water, the solution is circulated in the apparatus at 180°F. A solution of the dye is added and the package dyed in this bath at 250°F for one hour; thereupon it is rinsed, soaped and rinsed again and dried. An even clear red shade is reported.

Other examples refer to similar dyeing procedure with the yellow dye *CI* 802 (Quinoline Yellow KT Ex) or with the orange acid dye *CI* 161 (eg, Amacid Orange R) or with acid dye mixtures which produce a black shade.

Among the references cited by the Patent Office:

An article by Meunier in *Am Dyestuff Reptr* 42, 39-41 (1953), published after the application date of the current patent, mentions on page 41, col 1, high-temperature dyeing of Orlon acrylic fibers with bisulfite as a reducing agent in the cuprous-ion technique. Furfural or glyoxal may be used as substitutes for bisulfite.

SHRINKPROOFING WOOL WITH ALKYLATED METHYLOLMELAMINES —— Hydrous Oxides Added

A,2,04

USPat 2,702,258 (American Cyanamid Co——Amick——Feb 15, 1955)

The current invention is an improvement over the well-known Reissue Patent 22,566, assigned by Johnstone and Van Loo to the same Company. The older patent protected the means of application of alkylated methylolmelamines to render wool or wool-containing material shrink-resistant.

It has been observed that resistance to shrinkage and felting can be increased substantially by the application of alkylated methylolmelamines in which a water-insoluble metallic hydrous oxide has been incorporated. According to the examples, a hydrous oxide, such as that of Co, Zn, Ti, Al or Zr, may be dispersed in the resinous treating bath by the addition of water-soluble salt of these metals to a catalyst solution, eg, diammonium hydrogen phosphate or triethanolamine phthalate, and the addition of this mixture to the alkylated methylolmelamine adjusted to a pH of about 9. Hydrous oxides of Zn, Ti, Al or Zr are preferred because they are white. Whenever a colorless product is not required, however, other metals that form insoluble hydrous oxides, especially cobalt salts, may be used.

The process has to be conducted in such a way that from 2.5 to 15% of the melamine condensate and from 0.025 to 5% (preferably from 0.1 to 2.0%), calculated from the metal's weight, is deposited in the dry material.

Example: a methylated trimethylol melamine resin is neutralized with NaOH to a pH of 9 and concentrated in vacuo to a solid content of 80%, then dissolved in water; an aqueous catalyst solution containing diammonium hydrogen phosphate plus some hexamethylene tetramine is mixed with cobalt sulfate, whereupon the hydrous oxide is precipitated. The dispersion is added to the resin solution. Woolen skeins were impregnated with this liquid, squeezed to a pickup of 97.2%, dried at 80°C and cured at 140°C for 9 minutes. (Curing temperatures of 100 to 150°C are generally preferred.)

Shrinkage tests were carried out in a shaking machine. Loops of yarns, previously well soaked in Lux soap and squeezed, were agitated in the machine in a 1.0% Lux soap solution. The shrinkage results were as follows:

Material	After 10 minutes	Shrinkage (%) after 20 minutes	After 30 minutes
Nontreated	11.9	25.4	43.2
13% resin-treated	4.0	11.8	20.9
13% resin-treated plus $CoSO_4$ (0.1% metal)	0.4, 0.7, 1.5	0.7, 0.8, 1.5	0.9, 1.0, 1.7

Thus it could be proved that shrinkage control can be attained well by applying the melamine condensates as such, according to the Johnstone-Van Loo patent. But far superior results may be observed when hydrous oxide dispersions are added as advocated by the current process.

Among the references cited by the Patent Office:

Reissue Pat 22,566 (Am Cyanamid-Johnstone, Van Loo/1944): shrinkproofing of wool by impregnating with nonpolymerized methylated methylolmelamines and curing at 200-300°F.

USPat 2,200,164 (Am Cyanamid/1940): abrasive grit, wetted with a partially esterified polyhydric alcohol and bonded with a melamine-aldehyde resin.

USPat 2,476,939 (U S Gypsum Co/1949) describes a self-hardening powdered mixture of a water-soluble, melamine-formaldehyde condensate with an alkaline earth hydroxide, which insolubilizes the resin upon contact with water.

USPat 2,566,964 (U S Gypsum Co/1951): a water-soluble, fire-retardant coating composition containing a hardenable water-soluble aminoplast, an acid-reacting ammonium phosphate and pigments consisting of baryta, gypsum, lithopone, or the like.

News of the Trade

Alliance, B-U Expansion Underway

Expansion of production and research facilities is now under way at Alliance Color & Chemical Co, Newark, NJ, and Blackman-Uhler Manufacturing Co, Spartanburg, SC, divisions of The Andover Company. Announcement of the program was made by Harold W Rose, president of Andover.

Alliance Color & Chemical Co is erecting a new boiler house and machine shop. The construction contract was recently awarded to Peter F Redfern & Sons Co, Jersey City, NJ. The space formerly occupied by these units will be used to enlarge the Alliance laboratories and offices.

To provide for increased manufacturing and warehouse facilities in the South, Blackman-Uhler has acquired additional land adjacent to the tract purchased in August, 1954 when The Andover Company was formed by merger of the four companies, now operating as separate divisions: Alliance Color & Chemical Co, Alliance Chemical Corporation, Blackman-Uhler Co, and Blackman-Uhler Manufacturing Co. The companies specialize in the manfacture and distribution of Fast Colors.

PTI Alumni Weekend

The Alumni Association of the Philadelphia Textile Institute will hold its annual weekend next week, beginning June 14th with a softball game between the 1956 graduates and the alumni, starting at 6:00 PM. Following the game, a clambake is scheduled.

On Friday, the 15th, the annual golf tournament will be held at the Manufacturers Golf and Country Club, Oreland, Pa. Those not wishing to play golf, can take part in a baseball game or take advantage of the swimming pool. Luncheon and dinner will also be served at the club.

On Saturday, June 16th, the Alumni will return to the PTI campus for commencement exercises beginning at 11:00 AM, where Malcolm E Campbell, dean of the School of Textiles, North Carolina State College, will be the principal speaker.

As a special convenience for the visiting alumni, a limited number of rooms in the new Residence Hall will be made available for those wishing to spend the weekend on the campus.

Norman A Johnson

ADR Editor Honored at Testimonial Dinner

Norman A Johnson, editor of *American Dyestuff Reporter*, was honored on May 15th with a testimonial dinner at the Hampshire House, New York, NY, on the occasion of his twenty-fifth anniversary of service with Howes Publishing Co, Inc.

Mrs A P Howes, president, began the proceedings by proposing a toast in the memory of her late husband, founder of the Howes organization. Following this, Myron D Reeser, business manager of *American Dyestuff Reporter*, paid tribute to Mr Johnson's long and faithful service in his discussion of "Norman Johnson—The Man." Ernest J Finan, executive vice president, presented Mr Johnson with a testimonial gift.

Mrs Howes read a telegram of congratulation to Mr Johnson from the New York Section, AATCC, which he has served as secretary for many years.

Mr Johnson, secretary and treasurer and a director of the Howes corporation, has been editor of *American Dyestuff Reporter* since February, 1949, having been named to the post following the death of Dr Louis A Olney, who had been serving as directing editor. Prior to that time, Mr Johnson had served as managing editor since June, 1931.

He has been very active in the national and sectional affairs of AATCC, currently serving on the President's Advisory Committee, Publications Committee, and Technical Committee on Research. He is also a member of Textile Research Institute, New York Association of Business Paper Editors, Chemists' Club, and National Republican Club. Heading his list of hobbies is boating.

Cyanamid to Build New Aniline Plant

American Cyanamid Company will start immediate construction of a plant to produce aniline by a catalytic process at the site of the company's Willow Island, W Va, plant. Announcement was made on May 1st by V E Atkins, general manager of Cyanamid's Organic Chemicals Division.

The plant will have a rated annual capacity of 24,000,000 pounds. Design work has been completed, and completion of construction is scheduled for the fall of 1957.

The Willow Island Plant is located in Pleasants County, W Va, about 17 miles up the Ohio River from Parkersburg.

The new plant will use, for the first time, a fluid bed reactor and new catalyst in the manufacture of aniline from nitrobenzene by the reduction process. Units to be built in the plant will be for nitric acid, nitric acid concentration, sulfuric acid concentration, acid mixing, hydrogen, nitrobenzene and aniline.

Cyanamid's new Engineering and Construction Division will have line responsibility for this construction project, which has been designed by Chemical Construction Corporation. It is expected that a number of contractors and subcontractors in the area will participate in the construction.

Apex Moves Offices to NJ

Apex Chemical Co, Inc, has removed its sales and administrative office to 200 S First St, Elizabethport 1, NJ. The offices were formerly at 225 W 34th St, New York.

Dan River-Iselin-Jefferson Negotiations Confirmed

W J Erwin, president of Dan River Mills, Inc, stated on May 14th that negotiations have been in progress between Dan River Mills and representatives of Iselin-Jefferson Co, Inc, looking toward acquisition by Dan River Mills, Inc of Iselin-Jefferson interest.

Mr Erwin denied emphatically the report that any plan is under consideration whereby any person, group of persons or corporation would acquire control of Dan River Mills, Inc.

TI Conference on Static Electricity in Textiles

The Textile Institute will hold a Conference at Zurich, Switzerland, Sept 13-17 to discuss "Static Electricity in Textiles".

Papers to be presented will cover the following:

Friday, Sept 14—"Fundamental Work on the Generation of Static Charge", P S H Henry, British Cotton Industry Research Association

"Scientific Control by Means of Antistatic Agents", J Chabert, Centre de Recherches Textile de Mulhouse

"The Relation between Structure Dielectric Constant and Electrical Resistance of Fibers", J W S Hearle, Manchester College of Technology

"The Relation between Coefficient of Friction Conductibility and Quantity of Electricity Generated during Rubbing", G L M Quintelier, S A Fabelta.

Saturday, Sept 15—"Examples of Static Generation in Industry", D Finlayson, British Celanese Ltd

"Static Electricity in Textile Fabrics", J Boyd, Courtaulds Ltd, and D Bulgin, Dunlop Research Centre

"Antistatic Agents in Fiber Processing on the Cotton System", A G Beaumont, Courtaulds Ltd

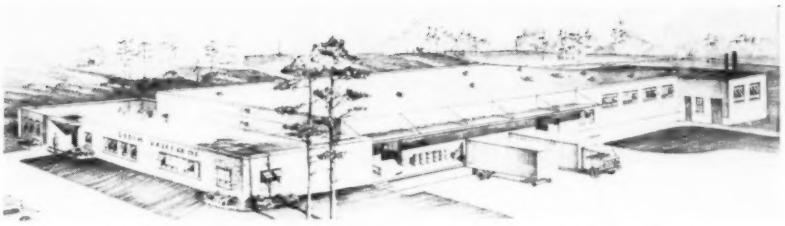
"The Use of Antistatic Agents in Textile Processing, with Particular Reference to Wool", J A Medley, Wool Industries Research Assoc.

Full details on the Conference may be obtained by writing to The Textile Institute, 10 Blackfriars St, Manchester 3, England.

New Scholarships at LTI

Lowell Technological Institute has been selected by Burlington Industries, Inc to receive one of the 2-year Burlington Industries Foundation scholarships, valued at $1000, payable $500 a year for the junior and senior years of the student chosen for the scholarship.

At the same time, the Institute has established a scholarship for the coming academic year in honor of the American Textile Machinery Association. Announcement of this scholarship was made at the TEAM (Textile Education and Machinery) Day Program, May 10, at which time the Institute was host to ATMA.



Artsits' conception of Stein, Hall's new facilities at Charlotte, NC

Stein, Hall Planning New Charlotte Facilities

Plans for construction of a new ¼-million dollar manufacturing plant, office building and laboratory at Charlotte, NC, have been announced by Lawrence Gussman, president of Stein, Hall & Co, Inc.

L Gussman

The new facilities, which will replace the firm's present Charlotte operation, will manufacture all of the products currently being made there by the Company. These consist of resins for a number of industrial applications and a variety of formulations for warp sizing, printing, finishing and other steps in textile production. In addition, it will turn out Stein, Hall's complete line of liquid adhesives. The expanded facilities also will make it possible to add other Company products as demand for them in the South increases and as new developments evolve from the research laboratories.

Construction of the plant will begin shortly and is expected to be completed by the end of 1956. The new structure will give the Company ample room for future expansion. It will contain 30,000 square feet of indoor manufacturing space, which will be augmented by some 5,000 square feet of outdoor process installations. Located near the Piedmont & Northern Railroad, the plant will have a 4-car siding.

Charles W Connelly & Associates of Charlotte has designed the new plant under the supervision of Stein Hall engineers, while the general contractor responsible for construction is R H Pennix Co, Gastonia, NC.

In addition to increased manufacturing and laboratory space the new structure will provide the Company with modern office space to house its Charlotte Sales Branch.

Fifth Annual Glycerine Research Awards Announced

The Glycerine Producers' Association has announced that the fifth annual Glycerine Research Awards are now open and that nomination blanks are available. This announcement was contained in a new bulletin describing the purpose of the awards, work eligible for consideration, method of nomination and judging, dates by which nominations must be received, and previous winners.

First award is $1000 and an honor plaque, second award $300 and third award $200. These awards are granted for independent research leading to new and improved applications of glycerine or glycerine derivatives to products or processes.

Copies of the bulletin giving complete details on the awards may be obtained from the Clycerine Producers' Association, 295 Madison Avenue, New York 17, NY.

NSP Renews Science Scholarships

National Starch Products Inc's continuation on a broader basis of its scholarship program in chemistry and chemical engineering was announced recently by Frank Greenwall, president. The schools involved are Columbia University, Case Institute of Technology, University of Nebraska, North Carolina State College, Syracuse University (N Y State School of Forestry), and Rutgers University. To aid the privately financed schools in defraying the administrative costs of these scholarships, the company has made additional contributions direct to these schools.

In addition to studying in the general fields of chemistry and chemical engineering, applicants must also need financial assistance and be of outstanding scholastic ability and high character. Recipients of the scholarships are under no obligation as to future employment with National.

LTI CHEMISTRY AWARD WINNERS—Chemistry award winners at Lowell Technological Institute, Lowell, Mass are congratulated by George R Griffin, chemistry division chairman, and Dean of Faculty Charles F Edlund. Left to right: Robert Davis '59, chemistry rubber handbook award recipient; Dean Edlund; Robert C Schiek, '57, Louis A Olney book prize winner; Dr Griffin; and Maurice Seifer, '58, Olney book prize winner. Chester Petkiewicz of Dracut, '56 also received an Olney book prize award.

GDGA to Meet at Tru-Color Dye Works

The Garment Dyers Guild of America's annual clinic and business meeting will be held June 8-9 in New York, with Tru-Color Dye Works, Inc, Long Island City, NY, acting as host plant for the occasion.

A luncheon is scheduled for 12:30 pm on Friday, June 8th, at the Oyster Bay Restaurant, with dinner slated for 7:00 pm in the Hartford Suite of the Hotel New Yorker.

Election of officers will be held at Friday's business meeting.

European Technical Digests

The best articles from European technical and industrial journals, translated and digested, are now available monthly to American industry, according to a recent announcement by John C Green, director, Office of Technical Services, U S Department of Commerce.

The Organization for European Economic Cooperation, a multi-government agency set up to stimulate economic growth of member nations, will distribute its monthly publication, *Technical Digests*, in the United States. It is designed primarily for those interested in manufacturing and production.

Many of the articles in the periodical, which averages 140 illustrated pages, discuss new products and processes developed by European manufacturers.

The Department of Commerce through its Office of Technical Services is cooperating with OEEC in making this new source of information known to American industry. Almost all fields of industrial interest are covered in the *Technical Digests*. Subscriptions are handled by the OEEC Mission Publications Office, 2000 P St, NW, Washington 6, D C. Rates are $24 a year or $2.50 per issue.

Booklet on Application of Textone

Detailed technical information on the application of Textone (sodium chlorite) in textile processing is contained in a new booklet available from Olin Mathieson Chemical Corporation.

The 16-page, file size booklet describes the use of Textone, a powerful oxidizing agent, in the bleaching of cottons and synthetic fibers, the oxidation of vat and sulfur dyes, and the stripping of nylon in hosiery-mill procedure.

The booklet may be obtained by writing on company letterhead to Industrial Chemicals Division, Olin Mathieson Chemical Corporation, Baltimore 3, Md.

7th Annual S-W Sales Conference

Developments and problems of textile finishing involving the use of rubber-covered rolls dominated the second day's panel discussions at Stowe-Woodward's Seventh Annual Sales Conference held at Brae Burn Country Club in Newton, Mass, recently.

In addition to discussions of new and unusual applications of rubber-covered rolls, Stowe-Woodward's sales engineers were provided with a working knowledge of the wide range of synthetic rubbers and the newer plastic compounds available for special extraction applications throughout industry.

Assisted by his staff, Warren Stubblebine, director of research and development, reviewed for the sales engineers both the laboratory and field research experience with these new compounds, pointing out the physical characteristics which recommended them for certain specific uses as well as their limitations.

General Calendar

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE
Gordon Research Conferences—Textiles Program, July 9-13, Colby Junior College, New London, N H.

AMERICAN ASSOCIATION FOR TEXTILE TECHNOLOGY, INC
June 6, Sept. 5, Oct 3, Nov 7, Dec 5 (All meetings at the Vanderbilt Hotel, New York, N Y).

AMERICAN SOCIETY FOR TESTING MATERIALS
June 17-22—59th Annual Meeting and 12th Apparatus Exhibit, Chalfonte-Haddon Hall, Atlantic City, N J; Sept 16-22—2nd Pacific Area National Meeting and Apparatus Exhibit, Hotel Statler, Los Angeles, Calif; Oct 16-19—Fall Meeting of Committee D-13 on Textiles, Warwick Hotel, New York, N Y.

THE DRYSALTERS CLUB OF NEW ENGLAND
June 22 (Outing Wachusett Country Club, West Boylston, Mass)

THE FIBER SOCIETY
Fall Meeting—Sept 6-7, Warwick Hotel, New York, N Y, Spring Meeting — May 1-2, 1957, The Clemson House, Clemson, S C

THE INSTRUMENT SOCIETY OF AMERICA
11th Annual Instrumentation-Automation Conference and Exhibit—Sept 17-21, New York Coliseum, New York, N Y

LOWELL TECHNOLOGICAL INSTITUTE
June 17—(Baccalaureate and Commencement Activities); Sept 26-28 (Perkin Centennial observance and open house). All events on campus at Lowell, Mass.

PERKIN CENTENNIAL
September 10-15. Waldorf-Astoria Hotel, New York, N Y.

PHILADELPHIA TEXTILE INSTITUTE
June 14 (Annual Meeting and Clambake—6 pm—College Campus, Germantown, Pa); June 15 (Outing—Manufacturers Golf & Country Club, Oreland, Pa); June 16(Commencement—College Campus—11 am).

THE QUARTERMASTER ASSOCIATION
Annual Convention—Oct 27-28, Conrad Hilton Hotel, Chicago, Ill.

QUEBEC SECTION, CANADIAN ASSOCIATION OF TEXTILE COLORISTS AND CHEMISTS
June 16 (Annual golf tournament).

SOUTHERN TEXTILE EXPOSITION
19th Exposition, Oct 1-5, Textile Hall, Greenville, S C.

SYNTHETIC ORGANIC CHEMICAL MANUFACTURERS ASSOCIATION OF THE UNITED STATES
June 12, Sept 11, Oct 9, Nov 7 (Palm Terrace Suite, Hotel Roosevelt, New York, N Y).

TEXTILE TECHNICAL FEDERATION OF CANADA
5th Bi-annual Textile Seminar—June 5-7, Queen's Univ, Kingston, Ont.

• NEW PRODUCTS AND DEVELOPMENTS •

Dextrol Scour SO-17

Scouring of nylon and acetate tricots and marquisettes in Burlington machines can be greatly improved, according to Dexter Chemical Corp, New York, through the use of a new low-cost agent, Dextrol Scour SO-17.

The product, the company says, is a completely emulsified, high-boiling, nontoxic solvent containing wetting agents and detergents. Because it produces an extremely fine solvent-emulsion in all dilutions, it is said to eliminate free solvent in the bath and residual odor in the goods.

Although this material also removes dirt and grease from fabrics processed in becks and jigs, Dexter reports that its effectiveness in the Burlington machine is enhanced by the fact that it does not foam.

A typical formula for scouring nylon tricot and marquisette, as given by the company, calls for 2% of Dextrol Scour SO-17 based on the weight of water in the Burlington machine and 0.3% of soda ash.

Cyanamid Announces Price Reduction for Melamine

A price reduction of three cents per pound for melamine was announced last month by American Cyanamid Company. At the same time it was announced that plans are being formulated for a major expansion of melamine production capacity.

The contemplated expansion would involve an 18-month construction program at Cyanamid's plant in Wallingford, Conn, to install facilities of 20 million pounds production capacity. This would be part of a larger expansion program, which has already resulted in a 20% increase in the melamine output of the Company's Willow Island, W Va, plant. Currently underway is construction of added facilities at the Welland, Ont, plant of North American Cyanamid Limited a Cyanamid subsidiary, which will increase by over 10% the plant's output of dicyandiamide, a raw material used in melamine manufacture.

The new melamine prices will be 30 cents per pound for carload or truckload quantities; 31 cents per pound for lesser quantities.

STANDARD BLUE JEANS are claimed to stay newer and neater looking for longer periods of time when made of the new Jet-Power Denim, a combination of American Enka's Jetspun solution-dyed filament rayon as the filling yarn with a vat-dyed cotton warp.

Developed in cooperation with the Lane Cotton Mills Division of M Lowenstein & Sons, this new denim reportedly offers greatly improved tear strength and abrasion resistance as well as a handsome appearance even after repeated washings.

Alpha Sulfo Alkyl Acids

Production of two sulfonic acids derived from palmitic and stearic acids is announced by the Chemical Division of Armour and Company. The alpha sulfo-stearic and alpha sulfo-palmitic acids are available in pilot plant quantities.

The sulfonated acids contain a strongly ionized sulfonic acid grouping and one carboxyl group, making possible a wide variety of normal and mixed derivatives such as alkali salts, amides, esters and alkyl ammonium salts.

Samples and a bulletin entitled "Alpha Sulfo Alkyl Acids" covering physical and chemical properties and other pertinent data are available on request by writing to the Market Development Department of the Armour Chemical Division, 1355 W 31st Street, Chicago 9, Ill.

New Application for Water-Skipper

Textile Adjuncts Corporation has announced that their new aerosol product, Water-Skipper, has been found to have a new application in textile mills, other than the recommended use of the product as a special on-the-spot water repellent.

The new use arose from tests that a few mills conducted on the company's recommendation, where drying cans and tenter frame clips and pins were treated with a light Water-Skipper application. Initial results reportedly have shown that light, thorough, and frequent Water-Skipper treatments on these metal units prevent resin build-up by reducing resin (sizing agent) deposit. It has also been reported that reduced heat transfer, induced by heavier coatings of high temperature plastics, is reduced to a minimum, or completely eliminated.

The use of Water-Skipper, an easy-to-spray, nonplastic aerosol product, also is said to eliminate the need to remove drying cans from the mill for expensive and delaying coating operations. A few simple rules have been developed for the effective use of this product, the main one being: metal surfaces have to be cleaned of previous resin deposit before an initial treatment.

Water-Skipper is being offered to mills by Textile Adjuncts Corp. with a money-back, satisfaction guarantee, when it is utilized for the application noted above.

Secondary uses for Water-Skipper include the spray treatment of calender and embossing rolls as an anti-friction agent. Knitting mills have also reported that the product offers promise in solving many loom problems.

Water-Skipper is an organic silicone-tung oil product that is packaged in pressurized 12-ounce and 3-pound disposable cylinders. It is also available in bulk form, uncompounded with gaseous propellent, for those desiring an economical substitute for organic silicone compounds.

Water-Skipper Technical Bulletin #WS-1-408 and a special application notice for this item are available from Textile Adjuncts Corp, 876 Pacific St, Brooklyn 38, NY.

Back numbers of American Dyestuff Reporter less than two years old may be obtained from Howes Publishing Co, Inc, 44 East 23rd St, New York 10, N Y at the following prices: 50¢ each, $7.50 for a complete volume in USA; 75¢ each and $15.00 per volume overseas. Earlier numbers may be obtained from the Secretary, American Association of Textile Chemists and Colorists, P O Box 28, Lowell, Mass. Prices postpaid: 50¢ each to nonmembers of AATCC, 35¢ to members; complete volumes $5.25 to nonmembers, $4.50 to members.

• NAMES IN THE NEWS •

Bintz

Klempner

The election of **Robert A Bintz** and **Lester Klempner** as assistant vice presidents has been announced by National Starch Products Inc, New York.

Mr Bintz for the past two years has been assistant to the vice president of manufacturing. Mr Klempner is now manager of sales for the Company's eastern division.

Joseph F Wildebush has been named executive vice-president of the Silk & Rayon Printers & Dyers Association of America by the directors, according to a recent announcement by Dean M Lewis, Colonial Piece Dye Works, North Bergen, N J, president.

Mr Wildebush has been vice-president-industrial relations, in charge of the Paterson office of the association. He will now direct activities at the New York office as well. He also is executive vice-president of the Textile Printers & Dyers Labor Relations Institute, sponsored by the SRPDA.

Mr Wildebush is an active labor arbitrator of the American Arbitration Association and lecturer on labor-management relations at NYU and Rutgers universities.

Edwin H Wolfe has joined the Antara Chemicals Division of General & Film Corporation as assistant manager of the Textile, Leather and Paper Chemicals Department and will direct his efforts primarily towards developing chemical sales in the paper and leather trades.

Mr Wolfe was formerly manager of chemical sales for Chemical Developments of Canada, Ltd.

Charles E Cooper, formerly with Allied Chemical & Dye Corp's National Aniline Division, has joined the Sales Department, Dyestuffs and Fine Chemicals Div, Harshaw Chemical Co, Hastings-on-Hudson, NY.

(Photo courtesy of Kenneth C Everett)

Raymond Curtis, (left), president of Kenyon Piece Dyeworks, Inc is shown receiving a suitably inscribed plaque from Fred Seiferheld, sales manager, at the Company's recent 20th anniversary celebration at Larchwood Inn, Wakefield, RI. April 26th, the day on which the affair was held, is also the birthday of Mr Curtis, one of the founders of the Company.

Others at the head table who spoke were: David Curtis, vice president; Raoul Archambault Sr, attorney; Eric Lee, comptroller; and Richard Seiferheld, N Erlanger, Blumgart & Co, who presented Mr Curtis with a clock. Master of ceremonies was J William Timperley, general manager.

The following persons have been chosen to receive Honorary Membership in The American Institute of Chemists:

Joel H Hildebrand, emeritus professor, University of California, Berkeley, Calif, and former president (1955) of The American Chemical Society;

Lawrence H Flett, New London, NH, former director of the New Products Division of National Aniline Division, Allied Chemical & Dye Corp, New York, N Y, and former president of The American Institute of Chemists;

W George Parks, head, Department of Chemistry, Univ of Rhode Island, Kingston, RI, and director of the Gordon Research Conferences.

The announcement was made at a luncheon meeting of the Institute, May 11, 1956, at the Hotel Statler, Boston, Mass, by the chairman of the Institute's Committee on Honorary Membership, John Kotrady of the Beacon Laboratories of The Texas Company.

Presentation of the certificates of Honorary Membership will be made at meeting dates to be announced later.

Herbert F Schiefer, a textile physicist in the Organic and Fibrous Materials Division of the National Bureau of Standards, has been awarded the Department of Commerce Gold Medal for Exceptional Service. The award recognizes his "outstanding contributions to textile science and technology."

Dr Schiefer has developed and invented many devices for testing the properties of fibers, yarns, and fabrics and a number are widely used by the textile industry today. He received the Harold DeWitt Smith Memorial Medal in 1950 from the American Society for Testing Materials for his pioneering work in textile research. His recent work has been concerned with new techniques for obtaining stress-strain relationships in yarns subjected to rapid impact loading and the measurement of a new basic property of textile fibers, the limiting breaking velocity.

Leon E Seidel, formerly associate editor of *Textile Industries,* has joined the Lurex Yarn Division of The Dobeckmun Co, with New York offices at 350 Fifth Ave.

Chapin A Harris, director of the Lowell Technological Institute Graduate School and head of the LTI department of fibers and yarns, has been selected by the University of Minnesota, which is handling the program for the International Cooperation Administration, to spend three months in Korea this summer to assist in the rehabilitation of Seoul National University.

Dr Harris will act as adviser to the textile engineering department and will be the consultant on setting up the revised and expanded textile program at Seoul University to accommodate the resumed needs of the textile industry and help it grow. He will leave June 4 and return in September, first undergoing an orientation period at Minnesota with **Prof Tracy F Tyler**, project coordinator.

At the present time **Prof Bum Shik Woo**, dean of students and head of the textile engineering department at Seoul University, and **No Su Kim**, instructor in dyeing and finishing at that university, are studying at Lowell Technological Institute under ICA auspices to obtain further training and experience in this country, where they will visit major textile research laboratories and firms and some of the other textile colleges before returning to Korea.

Four major appointments in the engineering section of the Silicone Products Department of the General Electric Company at Waterford, NY, have been announced.

The appointments are of **Stuart D Brewer**, manager-resin product engineering; **Frederick M Lewis**, manager-advance development; **Abbott Pozefsky**, manager-analytical and control methods unit; and **William F Gilliam**, specialist-technical information exchange.

John T Larsen has been named assistant manager of United States Testing Company's Denver laboratories.

He will assist **Berry N Duff**, manager of the Company's Western Division, in the processing of large-scale fiber testing, and in research in sampling and testing procedures.

William C Dodson, longtime Smith, Drum sales and development engineer, has announced his retirement as of May 1, 1956. Most of his time will be spent at his 85-acre farm on Currituck Sound, NC, although he plans to also maintain his residence in Meadowbrook, Pa.

On a consulting basis Mr Dodson will be "on call" by Smith, Drum and Company.

Brick

Jacobs

Schlesinger

In a realignment of its textile chemical sales responsibilities, **Leon P Brick**, executive vice president of Onyx Oil & Chemical Company, Jersey City, NJ, has been placed in charge of such sales in addition to his regular duties.

Other changes in the textile chemical staff include the promotion of **Paul D Jacobs** to assistant sales manager of the Textile Division. Mr Jacobs was formerly group leader of the textile evaluation and testing group.

Morton Schlesinger has been appointed to succeed Mr Jacobs in the Research Department.

Five district managers and two assistant district managers have been appointed for Carbide and Carbon Chemicals Company, a Division of Union Carbide and Carbon Corporation.

R A Corio has been appointed district manager for the Newark District and **M R Kleeman** has been appointed assistant district manager.

B A Gustin, Jr has been appointed district manager for the Boston District. He was formerly district manager for the Charlotte, NC, District.

R J Hughes has been appointed district manager for the Philadelphia District.

J F Luther has been appointed district manager for the Charlotte, NC, District. Formerly he was district manager for the Albany District.

J R Retter has been appointed district manager for the Albany District.

William Samson has been appointed assistant district manager for the Detroit District.

Dewey H Nelson, formerly Mid-West district manager for Becco Chemical Div, Food Machinery and Chemical Corp, has been promoted to assistant to the sales manager. He will make his headquarters in Buffalo.

James F Whalen, Jr, a Becco sales representative attached to the Southeastern district office in Charlotte, has been appointed Mid-West district manager in Chicago to succeed Mr Nelson. **Edward A Dalmas** has joined the Charlotte sales staff, replacing Mr Whalen.

J A Robertson has been named supervisor of chemical microscopy at FMC's new central research laboratory now under construction near Princeton, NJ. Since 1943 he has been engaged in the application of optical microscopy to research problems at FMC's Westvaco Mineral Products Div, Newark, Calif. He will move to Princeton when the new facilities become operational this summer.

Ross M Sims has been appointed plant manager in charge of all operations of the Moundsville, W Va, Plant of National Aniline Division, Allied Chemical & Dye Corporation.

Plant Superintendent since May, 1953, Mr Sims has participated in the rapid expansion of National Aniline's operations and facilities in the Moundsville area.

Prior to his Moundsville appointment, Mr Sims had served in various capacities in National Aniline's Buffalo, NY, Plant since 1944.

Three superintendents of engineering have been appointed by National Aniline—**D A Feil**, at the Chesterfield, Va, Plant; **D A Aubrecht**, for the Moundsville, W Va, Plant; and **William M Holtzclaw**, at the Buffalo, N Y, Plant of the Company.

Bette Davis, Lowell-born, two-time Academy Award winner and first and only woman president of the Academy of Motion Picture Arts and Sciences, was at Lowell Technological Institute on Friday, May 4, to receive the Lowell Tech Players award during its presentation of "Mister Roberts." **Gary Merrill**, star of stage, screen, and television, accompanied his wife to the play. Frederick Obear, president, who was seen in the title role that evening, made the presentation.

Miss Davis was honored by the Players as first recipient of the award for her significant work and interest in the little-theater movement and college dramatic groups.

The Tech Players group this year is observing its 50th anniversary as the dramatic society of the engineering college.

Brown

Croghan

Feeley

Haley

Edwards

Claud Brown has been elected a vice president of Interchemical Corporation and will continue to hold the office of treasurer.

Mr Brown joined Interchemical in 1930 as a member of the comptroller's office. He was elected comptroller of the Printing Ink Division in 1938 and a division vice president in 1948. He has been Interchemical treasurer since 1951.

Jackson Bauer recently accepted a position in the Research Division of Collins & Aikman Corporation to work on special research assignments in fiber processing. The Research Division of C&A will have its headquarters in Downingtown, Pa.

Mr Bauer was formerly vice president in charge of research at Fred Whitaker Co, Philadelphia, Pa, having been with this company for 17 years. Mr Bauer has developed processes for wool scouring, carbonizing and dyeing as well as numerous processes involving synthetic fibers.

In line with its expansion of West Coast activities, the Nopco Chemical Company has appointed **D E Murphy** as a new member of its technical sales staff.

Mr Murphy is the fourth technical sales representative added to the staff in the past year. He has been assigned to the Southern California sales district, and will make his headquarters in Los Angeles.

Frank M Croghan has been named manager of personnel relations of the Linden, N J, dye and chemical products plant of General Aniline & Film Corporation. Mr. Croghan succeeds **E Rabun Swint** who was recently named manager, executive development for the Company's Dyestuff and Chemical Division.

Mr Croghan joined General Aniline as labor relations supervisor at Linden in 1953 and since May 1955 was assistant manager, personnel relations.

E J Feeley Co, Boston, Mass, has announced the promotion of **E J Feeley II** to the position of vice president, and **C F Martin, Jr** to the position of Southern sales manager. Both men will continue to make their headquarters at the Company's branch warehouse and manufacturing facilities in Charlotte, NC.

Bernard Menin has been appointed manager of the Textile Sales Department, and **Robert K Smith,** manager of research, for E F Houghton & Co, Philadelphia.

Mr Menin, who was formerly assistant manager, succeeds C B Kinney, who retired in March after more than 25 years with the Company.

Dr Smith was formerly associated with the Houdry Process Corp, Marcus Hook, Pa, as chief of the Exploratory Research Section.

H Russell Haley, a representative for Onyx Oil and Chemical Co for more than sixteen years, has joined the sales staff of Emkay Chemical Co, Elizabeth, NJ.

Frederick J Edwards has been named assistant advertising and sales promotion manager of American Cyanamid Company's Industrial Chemicals Division.

Mr Edwards will also serve as advertising manager of the Division's Paper Chemicals Department and the Refinery Chemicals Department.

He was formerly a staff executive of the American Association of Advertising Agencies.

Ernest St Louis has joined the Finishing Plants Division of United Merchants and Manufacturers, Inc, as director of chemical manufacturing.

Mr St Louis will supervise all chemical manufacturing for the Finishing Plants Division and will make his headquarters at the Southern Textile Chemical Corporation Plant, located at Clearwater, SC. He will also be director of the Chemical Manufacturing Laboratory, working on the development and introduction of new products for the Finishing Plants.

Mr St Louis was formerly with Synthron, Inc as development director. He was also connected with Warwick Chemical Company as research chemist and technical service manager.

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